THE JOURNAL
OF THE
AMERICAN LEATHER CHEMISTS ASSOCIATION

VOL. LII JULY 1957 No. 7

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The Journal

of the

AMERICAN LEATHER CHEMISTS ASSOCIATION

Vol. LII JULY 1957 No. 7

CONTENTS

pH in Leather Making - - - *By* H. G. TURLEY **354**

Some Notes upon Hide and Leather Quality Interrelationships - - - *By* R. HAUCK and R. M. LOLLAR **361**

Creep Rupture of Leathers under Tensile Loads - - - - - - - - - - *By* D. H. RUSSELL **396**

Life Lines - - - - - - - - - - - - **401**

ALCA News - - - - - - - - - - - **402**

Abstracts - - - - - - - - - - - **405**

Cover—Milton Park Laboratory of the British Leather Manufacturers' Research Association.

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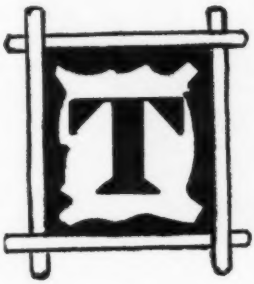

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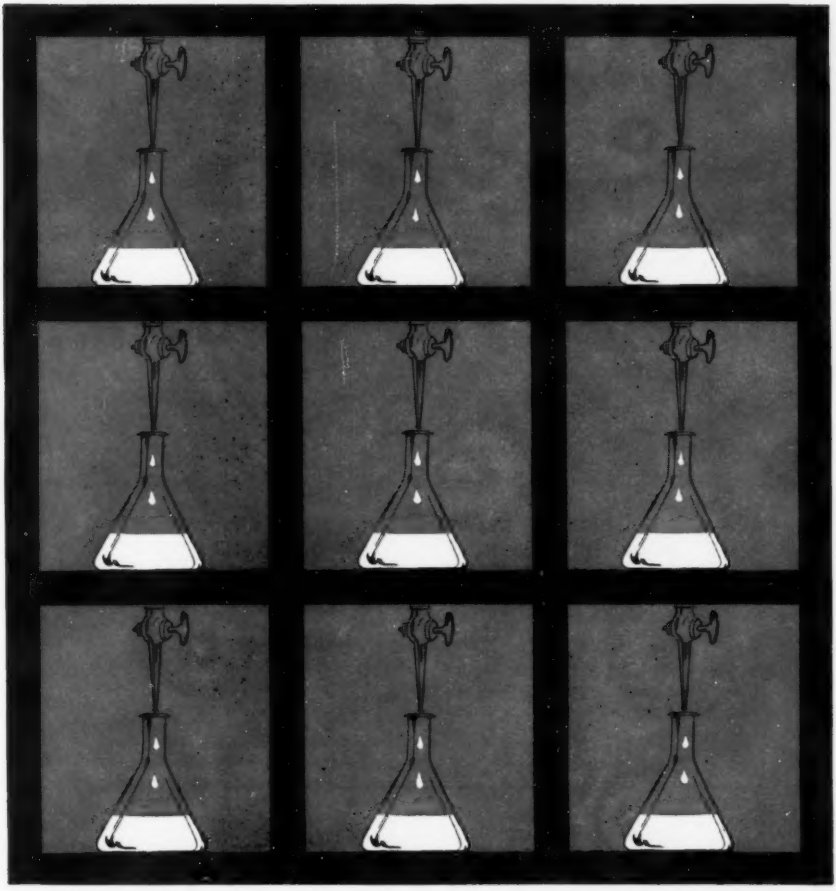

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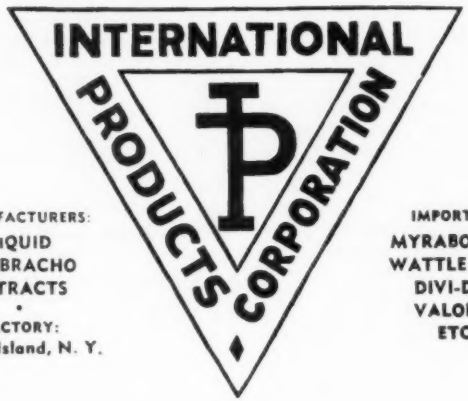

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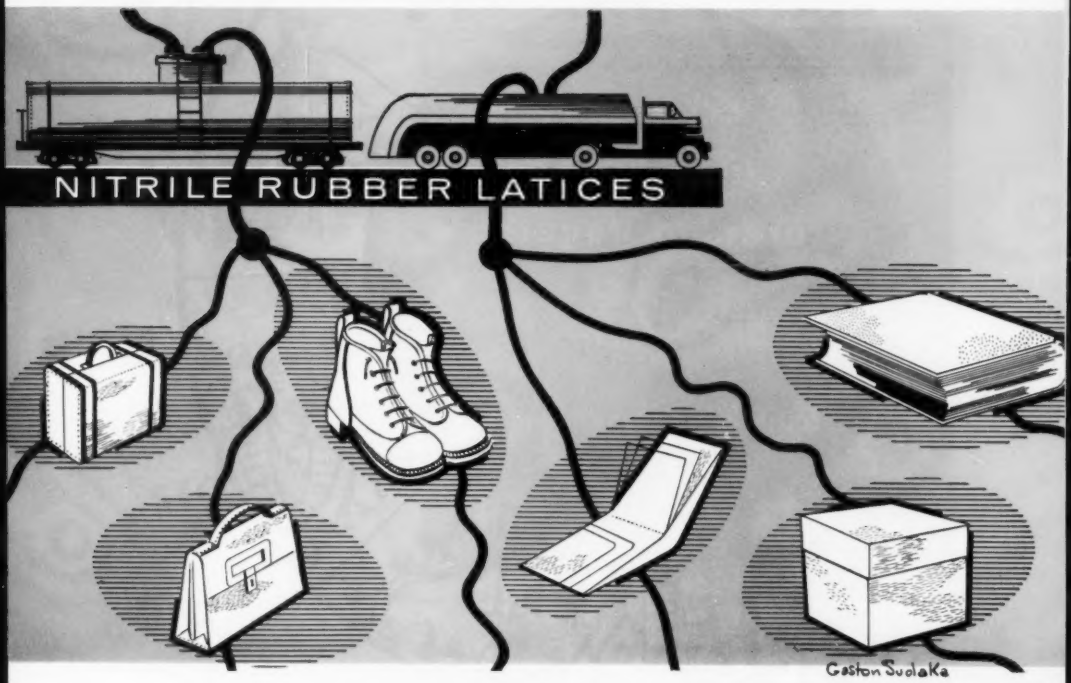

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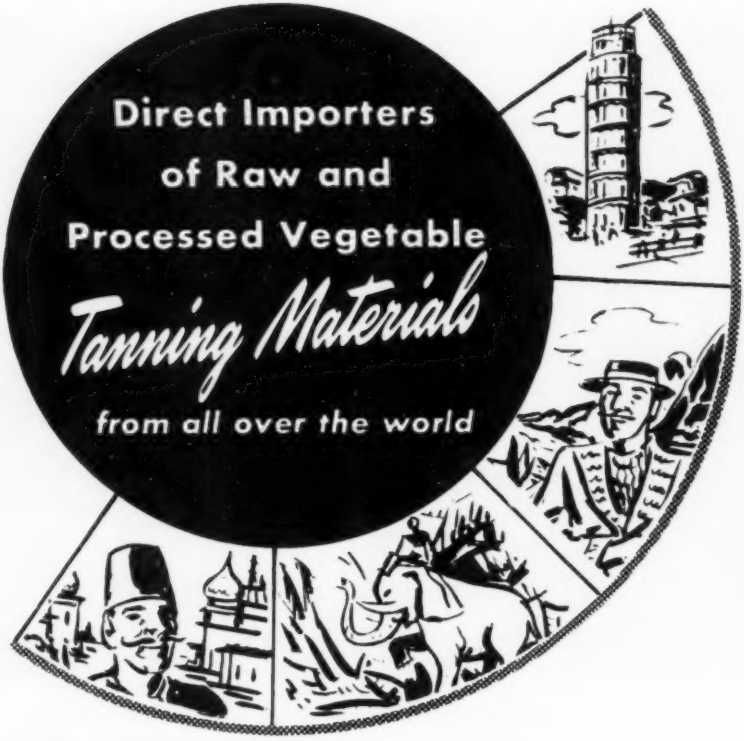

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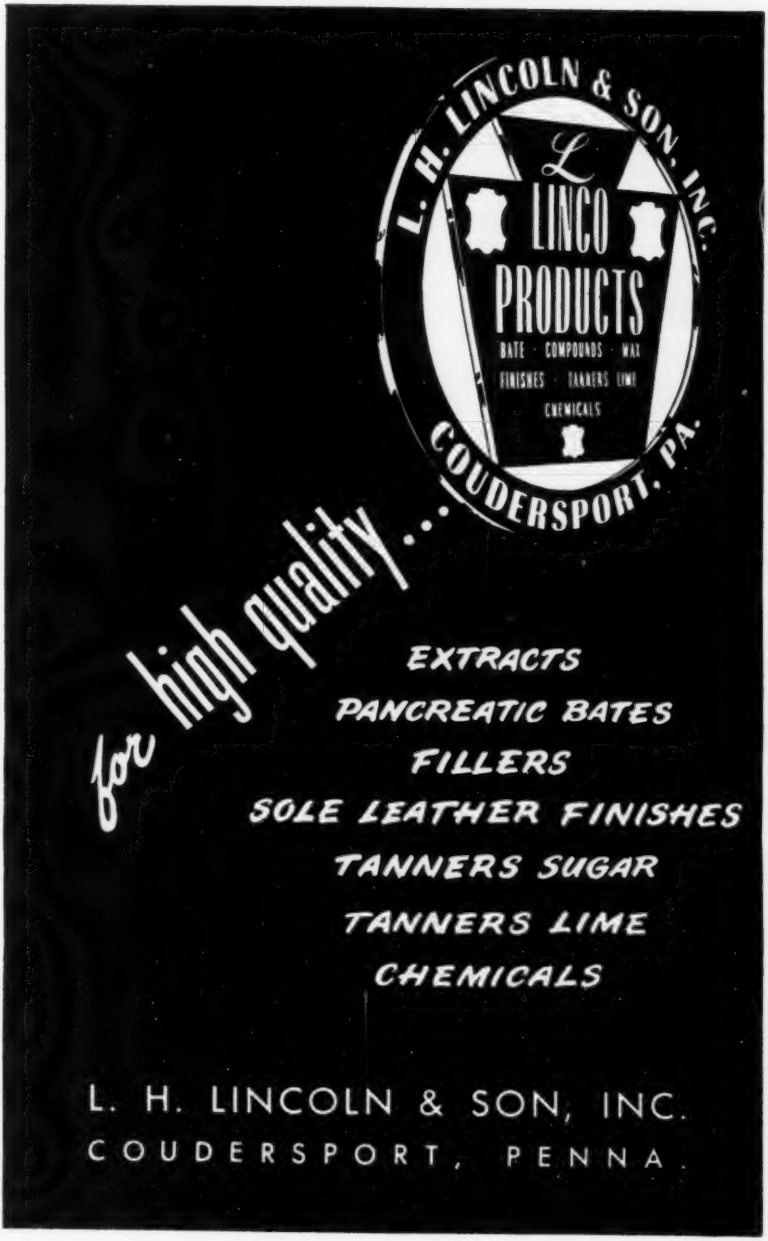
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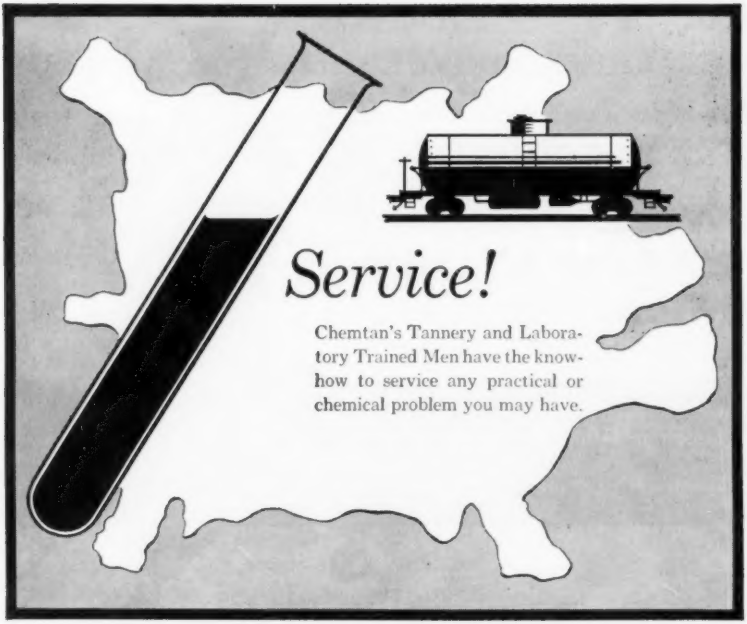
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General correspondence concerning the *Journal* should be mailed to the Managing Editor.

Subscriptions—$12 per year for members; $15 for nonmembers.

pH IN LEATHER MAKING*

H. G. Turley

Rohm & Haas Company
Philadelphia, Pennsylvania

ABSTRACT

The significance of the pH value of the skin fibers, as opposed to the pH of the liquor, is emphasized. Examples are cited where the external solutions—bate liquors, pickle liquors, or vegetable tan liquors—may have the same pH value but where the character of the leather may be affected radically by differences in pH value in the interior of the pelt.

With the development of modern electronic equipment using the glass electrode the measurement of pH today has been made effortless and commonplace. Herein I believe lies a certain danger—it is possible that too much reliance is commonly placed on pH measurements, particularly of liquors, to control leather production, with a tendency to forget the often larger factors of the quantities of materials involved. We propose to draw attention to the acidity condition of the skin or hide fibers rather than to the reaction of the solutions involved.

In 1931 S.P.L. Sorensen (1) gave a talk at the Leathersellers' Hall in London. He pointed out that pH determinations were of value in such industries as brewing, distilling, yeast making, baking, dairy products, and leather factories. He had this to say about leather: "In leather manufacture the problem is one of the different behavior of various proteins and the action of chemical or enzymic decomposition. It is therefore obvious that in this industry it is of the greatest importance to secure a close regulation of the hydrogen-ion concentration during the various processes so that the whole process can take place in the best possible manner." By 1931 pH was commonly used in the leather science literature and had begun to be used in a practical way in the tanneries.

In brief historical outline we have:

1900–20—pH was first defined, and accurate methods for measurement were developed.

1920–30—pH measurements by indicator and hydrogen and quinhydrone electrodes were brought to a high state of perfection.

1930–40—Glass electrodes were developed.

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In the recent ALCA practical leather making symposium pH has been mentioned somewhat, and it was briefly pointed out that "you can even be oversold on the effect of pH in some operations . . ."

It is realized that the important operations of leather making are conducted in their own somewhat restricted pH range. This has been mentioned in the literature, but briefly. The pH ranges likely to exist in manufacturing leather are given in Figure 1. Sometimes there are exceptional processes which

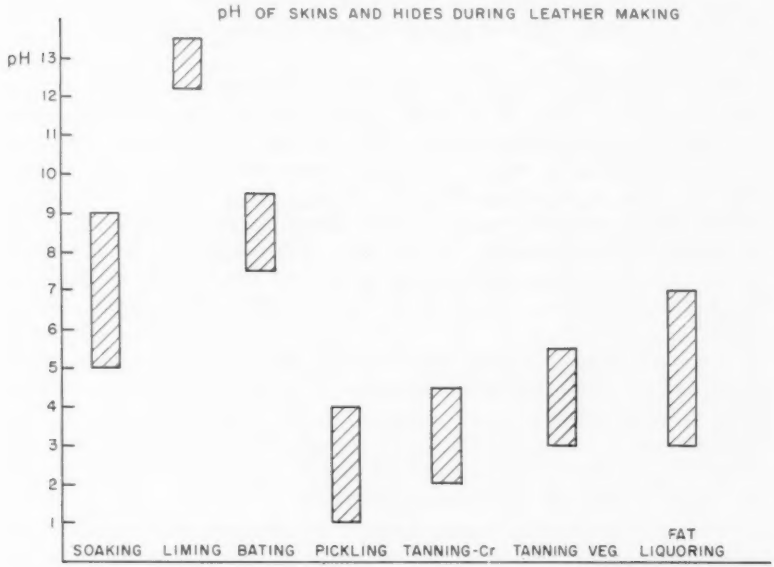

FIGURE 1.

may depart from the ranges given, but in general these are the ranges for the different processes. Actually the whole pH scale may be covered at some point or other in making a piece of leather. These figures refer more especially to the spot pH of hides and skins and not necessarily to the liquors. That there may exist a differential pH in different layers of the skin is commonly experienced and is discussed later in this paper.

It is now pertinent to ask, Where do we stand today? Methods for measuring pH have been developed and refined to a point where it has been stated that taking the pH is as effortless and simple as taking a temperature. The development of the colorimetric method has been so refined that we have excellent, handy, practical apparatus today that can be kept in the pocket and taken directly into the tannery to the actual location of the liquors and

solutions. By comparing the colors obtained with indicator standards in a glass tube or revolving colored glass standards the pH of the liquor can be obtained certainly to 0.2 of a unit. Further, in place of the old litmus paper which was a standby for many years we now have dozens of pH test papers to cover any range, and by suitable choice of paper the pH measurements are accurate to about 0.2 pH unit. The electrometric pH by glass electrodes has been highly developed and refined to a point that it is now used in all industries. Even here the latest development is a small pocket glass electrode which can be taken to the side of the paddle or vat and is accurate to 0.1 pH. It would therefore seem that our difficulties with measuring pH are over.

The determination of pH provided the leather research workers with a fine tool in the 1920's. It was even thought by some outstanding leather scientists that by knowing the pH of liquors and solutions we would have leather making under strict control and would arrive at a Utopia where there would be no serious problems in making leather. We have had many articles embellished with many curves of pH of liquors or solutions. Some of us were duly impressed with this work, but others of us found it difficult to interpret the data in terms not of liquors and their acidity or alkalinity but of leather qualities. Unlike some industries where pH has been of great significance, in which the product is a solution such as beer, wine, soft drinks, etc., in leather making we are fundamentally dealing with a solid material, the skin fibers. This is further complicated by the fact that it is a very wonderful material, responding to changes in acidity and alkalinity in a way that influences greatly the quality of the resulting leather. It is realized by most of us that it is not a simple question of soaking, unhairing, bating, tanning, and so on, but how we conduct these processes.

It is perhaps somewhat surprising that in the scientific literature there has been relatively little published to stress the importance of the pH condition of the skins in tanning. In 1931 there appeared what I believe to be an important article by G. Peace (2) in the *Journal of the International Society of Leather Trades Chemists*, "On the Importance of the pH of the Pelt in Vegetable Tanning". I would like to quote from this article as follows: "If we take into consideration the amount of attention that is now paid to the pH of the tan liquors themselves, it is very surprising that so little care is given to the pH of the pelt before commencing the tanning operation proper. In part no doubt this is due to the fact that so many pH researches in the leather trade are made on hide powder and in part to the assumption that the hides may be readily adjusted to the pH of the liquors they are in while tanning is proceeding". Peace goes on to point out that when a hide containing an internal streak of high pH is put into an acid tan liquor the surface of the hide may be reduced to a low pH with a consequent heavy deposit of tan in the grain layer before any tan can penetrate into the interior.

Before the pH of the center of the hide has reached the pH of the solution, the surface layers are so heavily tanned that penetration is very slow. Also, owing to the production of a dark, hard grain, the leather is liable to crack, and extra processes have to be adopted in finishing it to correct the ill effects produced in the early stages. This, for example, has led to the use of heavily bisulfited extracts and even to adding bisulfite to reduce the ill effects of the unnecessarily added acid. The swelling of the hide, according to Peace, depends not so much on the acidity or the pH of the liquor it enters as on the pH to which the hide fibers themselves are brought. In other words, while it is necessary that the tan liquors themselves have the best pH for the type of tannage required, the fundamental factor is the pH of the hide fibers themselves when tanning occurs, for unless this pH is right, no satisfactory leather can be produced. The appreciation of this led Peace to patent a process which is extremely important from the point of view of rapid vegetable tannage. This process, British Patent 344 417 of November 27, 1929, "Improvements in Process for Preparing Hides and Skins for Vegetable Tanning" (3), states that prior to tanning, hides or skins are treated with solutions of salts of weak acids and mineral acid or the equivalent of the weak acid, such as sodium acetate plus acetic acid, in order to bring the pH uniformly to 3.5 and 5. The pH of tanning liquors should be held at 3.5 to 5 until the hides are struck through. The type of tanning is short, and the use of strong liquors is unnecessary. This concept has been of great value in the vegetable tanning of sole, belting, harness and strap, and upholstery leather. By bringing the hide—the whole hide, the center as well as the surface—to the pH of the tanning liquor with a buffer such as acetic or formic, the vegetable tans penetrate quickly and uniformly, and no time is lost. In this way the speeding up of the tannage of sole leather and upholstery leather is achieved. It is therefore quite like the work that has been done in chrome tanning with the formate tannages. However, I would point out one considerable difference: in the vegetable tanning the completeness and fullness of vegetable tannage may make up for a certain amount of initial softness and emptiness of the hide structure which is not compensated for in the relatively light chrome tannage.

I believe we have now arrived at the point where we shall be forced to pay more attention to the acidity, neutrality, or alkalinity of the skins, which governs their electrical charge, and which we might call for the present, even if erroneously, the pH of the skins. Compared to solutions it is not an easy matter to be able to measure the pH of the skins.

For thirty years we have been "spotting" the skins with pH indicators and judging the condition of the skins by the colors obtained on a cut surface. The color given by the skin has been matched against the pH color of the indicator, and we have called this the pH of the skin. This has been criticized as being merely a measure of the pH of the solution in contact with the skin

at the different points, such as the center, compared with the grain or flesh. In working with this, however, we have gained the impression that it is in a way a measure of the actual pH condition of the skin. We would like to confirm this by simpler measurements with glass electrodes, but this is difficult. By placing the reference cell and glass electrode on the surface of the skin we can get a pH reading which probably represents the general area of the skin. However, when we come to the cross section, our apparatus at present is too clumsy. We would like to have further refinements in this type of apparatus, and we would literally like to pinpoint the different areas by a tiny glass electrode having a contact surface no greater in area than the head of a pin. Perhaps such equipment can be designed.

That the so-called pH of the skin, particularly the internal layers, is more important than the pH of the external liquors can be illustrated by a few examples. I believe some of the processes where the internal condition of the skin is important and may be quite variable are bating, pickling, chrome tanning, neutralizing, dyeing, and fatliquoring. The problem is important nevertheless in all phases of leather making, but in those enumerated it is especially obvious.

Take bating—we may bate skins in two different ways and have the external liquor at a favorable point, say pH 8.5–9, yet the internal condition of the skins may be quite different. In one case we may have complete deliming and a uniform pH of the skin, and in the other case we may have anything but complete deliming with quite a considerable internal layer at a pH much higher than the bating solution, even pH 11. Will there be any differences in these leathers produced? There certainly would be if no further compensations were made in the succeeding processes. In the one case the tendency would be to have a thinner, flatter, more stretchy leather and in the other case a fuller, more compact, solid leather. If the second example were not handled carefully later on, we might have a distinct tendency toward poor break, because in essence we really have two kinds of leather cemented together—a soft one on top of a firm one—, and this would provide ideal conditions for producing a poor break. Therefore, tanners in discussing their problems might be quite confused about making the same type of leather. They both maintain the same liquor pH yet have quite different types of problems with their leathers.

Now take pickling—here there seems to be much argument. Again, the same external pH may be produced, but the resulting leathers may be quite different. We could visualize three simple operations. Let us take, for example, the pH 3.0 of the external liquor. In the first case the use of a small amount of sulfuric acid on a well delimed skin may produce a uniform pH of the skin, leaving very little sulfuric acid in the external solution. pH 3.0 would be a solution containing 7 ounces of sulfuric acid per 1000 gallons. Such a small quantity of acid would have very little effect in changing the com-

position of the tanning solution employed. Secondly, we have the case where the pH of the external solution is 3.0 prior to the tannage, but based on the previous amount of deliming and the time of pickling the pH of the interior of the skin may be quite different, perhaps as high as 7.0. On chrome tanning, the external acid being very weak will have practically no effect on the chrome tanning solution, but when the chrome solution after penetration of the grain or flesh surface comes to the layers of higher pH in the center of the skin, the basicity of the tannage is changed, and there is a quick deposition of a more basic tannage with a distinctly different color, often many shades of blue darker. Here again we virtually have two leathers cemented together, a grain leather of low-basicity chrome tannage and an internal leather of high-basicity chrome tannage. In the case of heavy skins, the flesh side of such a leather, when split, shows un-uniform dark-colored areas and has a different feel or physical condition. When this condition is bad, it may even give trouble in splitting. I have noticed in different tanneries, particularly side leather, that in the past ten years there has been good progress in this direction. Not all but many leathers are now made uniform in the chrome-tanning operation. After splitting they present a fine uniform surface, uniform color, and uniform fibers from which to manufacture good-looking suede leathers. The tanner of "splits" purchased in the chrome "blue" conditions is often plagued with these different variations and the character of the splits obtained from different tanneries.

In the third case the tanner may obtain quickly a uniform pH of the external solution and of the internal layer of the skin by the addition of a buffer salt such as sodium formate, sodium acetate, etc. In this case it must be remembered that in the external solution we now have considerably more acid, in this case formic acid or acetic acid, and more sulfuric acid in the pickle. This formic acid reacts at once to change the composition of the chrome tanning solution. The pH is raised and the strong acid neutralized, so that we no longer have the simple basic chrome sulfate but very often a mixture of chromium sulfate and chromium formate. This tannage proceeds smoothly and rapidly, and because there is no differentiation of internal layers of the skin, the leather is apparently uniform. However, it may not have the same physical characteristics as the simple unbuffered chrome sulfate tannage. It has characteristics which may be better or poorer than those required in the particular leather being made. There is a tendency toward a softness of leather which may not always be desired. If this softness is too prominent on the grain, it may be necessary to counteract it by further treatment of the grain area with such filling agents as vegetable tans and synthetic resins. So we have three cases where the usual pH of the pickle liquor is the same, yet varying results of leather quality may be produced.

Another area for pH control is in the important step of neutralizing chrome leather. This is frequently done by the addition of a small amount of alkali

salt such as sodium bicarbonate, although many similar materials have been and are being used. According to the quantity of bicarbonate used and the time given for it to reach equilibrium we may again have different results. In taking the first chrome leather described above, which is very uniform, out of tan, we may produce a relatively alkaline layer on the surface of pH 5 or even 6.5. We have again made unconsciously two types of leather—a somewhat basic leather cemented to a more acid leather. The basic leather would tend to be soft and fuller and could "break" more easily. Such a leather could change in varying degrees the dyeing properties in one and the same dyeing formula and in turn affect the fatliquoring operation by influencing the penetration and distribution of the emulsified oils. If the effect of the fatliquoring is to compensate for the effect in neutralization, we have a very fortunate situation, and we have a good product. However, if they are not in harmony, then there can be slight variations from pack to pack from day to day, and we have produced a certain amount of nonuniform leather which will show up on the grading and sorting table.

The question of pH in leather making is a big topic and cetainly can only be touched on in a short discourse. The fundamental point I wish to bring to your attention is not new but is one which I believe even today commonly is not given enough consideration. This is the cardinal point of pH not with respect to liquors but with respect to skin fibers. We need to pay more attention to this, particularly when dealing with heavy stock, and this idea is of great importance to the side leather tanners and the sole leather tanners. When we keep this factor in mind, it is often relatively simple to modify our processes so that we approach, even if we do not realize completely, equilibrium conditions. In my experience, when we do this, we do not have to think so much of making compensating changes in later stages of leather making, and in a more practical way we can produce better leather. Sometimes the changes required are trivial, for example, merely running a process for one hour instead of half an hour, etc. In some cases even shortening the process is all that is necessary. As we progress we should, I believe, have better equipment for the accurate measuring on the spot of the pH values of the internal layers of hides and skins. At the moment the best we can do is to spot with pH indicators.

In summation, we urgently advise you to "Watch the skins and keep an eye on the liquors, but don't forget the skins."

REFERENCES

1. Sorensen, S. P. L. *J. Soc. Chem. Industry*, **50**, 278T (1931).
2. Peace, G. *J. Intern. Soc. Leather Trades' Chemists*, **15**, 22 (1931).
3. ———, *Ibid.*, 300 (1931); Brit. Pat. 344-417, Nov. 27, 1929.

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SOME NOTES UPON HIDE AND LEATHER QUALITY INTERRELATIONSHIPS*

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ABSTRACT

Two hundred sides of chrome-tanned side leather and the hides from which they were made have been examined to secure information on the contribution of various characteristics of the cured hide to the quality of the leather. Despite the sensitivity of a paired-side experiment in which alternate sides of the same hides were subjected to salt curing before and after a 48-hour post-mortem delay at 65°–70°F. no significant difference was noted in the hide inspector's evaluation of the cured sides or in the leather inspector's evaluation of the final leather. The most significant factor contributing to the physical properties of the leathers was their content of hide substance, and it is suggested that tanners should be more concerned about the content of leather-making substance in the hide lots which they purchase. It should not be generalized from these experimental results that careless practices in the handling of flayed hides during curing and storage cannot produce undesirable results observable in the quality of the final leather. It is, however, emphasized that the estimation of the leather-making potential of a lot of cured hides is a very complex subject, and it is hoped that the publication of this article will stimulate further thinking and study of the subject so that adequate quality control specifications on cured hides can be written at a later date.

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INTRODUCTION

Efficient curing is necessary to preserve the extremely vulnerable skins or hides from the time of flaying until they can be worked into the tannery beamhouse processes, since only well preserved skins and hides can be made into acceptable quality leather. Many variables have been suggested as factors that are concerned with the quality of cured skins and hides. However, studies on the interrelationship between cured skin and hide quality

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and the quality of the resultant leather have not been reported very frequently. Most information on the subject, since it is the result of practical experience, is largely subjective and intuitive. Although tannery chemists have conducted extensive studies of the interrelationship between hide and leather quality, these studies are largely unpublished. Therefore it is very difficult to define an adequate quality control specification for cured skins and hides which will give a high level of assurance that good-quality hides are being presented in a given commercial lot.

This article examines some factors that are thought to be related to the correlation between the quality of green-salted cattle hides and their potential leather-making quality. These observations are based on an examination of the literature and on certain preliminary experiments that we have conducted. This article is presented in the hope that it will stimulate the necessary work to make it possible to write improved quality control specifications for cured skins and hides.

SOME PRINCIPLES OF CURING

Hausam has reviewed much of the curing literature which appeared between 1927 and 1949 (13, 14). These two articles are very valuable since they present in outline form the information on the several factors which are concerned with curing with sodium chloride. The first article (13) emphasizes that salt-curing should follow immediately after removal of the body heat from the skin or hide, the correct time being four to six hours after flaying. Earlier, McLaughlin (22) had shown that the ability of freshly flayed hide corium pieces to swell in lime solutions was decreased by post-mortem periods as short as 1.5 hours. Further, McLaughlin and Theis (24) observed that post-mortem periods of 1 to 6 hours resulted in a decreased initial rate of salt diffusion into the hide either from a 25% NaCl brine or from green-salting. However, these workers did not report directly on the "extent to which these post-mortem changes in hides and skins affect the quality, quantity or cost of leather produced (since these are to) be proved by a practical experiment. Such experiments are now under way" (22). However, the reports on these experiments were not published due to a tannery fire; it is unfortunate that the experiments were not repeated at that time.

Kaye (15) published the results of a microscopical study of the effect of post-mortem changes on hide structure in an article similar to an earlier private publication by Jordan Lloyd (15). Post-mortem changes are divided into two types: putrefaction, which results from bacteria attacking the hide tissues after flaying; and autolysis, which includes the enzymatic hydrolytic deterioration of the cellular tissues of the hide and occurs even though the skin or hide is clean and free of bacteria. Changes in the condition of the hide structure during post-mortem periods of 0.25, 5, 11, 32, 52, and 192

hours at 20°-22°C. were studied in detail microscopically for the different structures in the hide. Pieces allowed to stale for 52 and 192 hours were judged to be partly putrefied, as indicated by odor, hair slip, and microscopic examination. The pieces that had been subjected to the various post-mortem periods were then placed in brine solutions containing 10, 15, 20, and 30 (saturated solution) % NaCl and held for periods up to three months. Other pieces were green-salted and then similarly stored. Pieces cured with saturated brine (or even in brine solutions as dilute as 23%) were similar in microscopic appearance to those which were salted. Pieces subjected to a 32-hour post-mortem period seemed to be intermediate in their reaction to storage after brine-curing or salting. These curing methods were able to retain the quality of the pieces subjected to post-mortem periods of 11 hours or less, but they permitted further deterioration in the pieces staled for 32, 52, and 192 hours before being cured. However, no evaluation of the cured pieces was made except for the microscopic evaluation.

Stather and Sluyter (34) compared on a laboratory scale the vegetable-tanned leather yields secured from hide pieces subjected to their usual 5-hour post-mortem period to the yields from pieces subjected to a 24-hour post-mortem period at 18°C. prior to curing. A 24-hour brining followed by salting comprised one cure, while a second cure involved green-salting followed three days later by resalting. Curing was continued at 16°-20°C. for one month for both types of cure following the 5- and the 24-hour post-mortem periods. The four sets of pieces gave equivalent white-weight gains and dry-leather weight yields after a twenty-day vegetable tannage.

Stather and Herfeld (35) extended this work, comparing immediate curing to curing after 24 and 72 hours of post-mortem time at 18°C. and 70% relative humidity. The results secured from the pieces held 24 hours prior to curing were equivalent to those from pieces cured immediately, while the pieces held 72 hours showed deterioration. The deterioration at this longer post-mortem time was so extensive that saturated brine was unable to prevent further deterioration during cure. The final salt uptake of the brined and the green-salted pieces was equivalent in amount and in distribution regardless of the post-mortem period. However, the 72-hour post-mortem period increased the rate of salt permeation with each type of cure, while the 24-hour period was without influence. As Hausam notes (13), these results are contrary to those reported by McLaughlin and Theis (24). The cured pieces were stored for 10 weeks and then subjected to beamhouse treatment. The 72-hour post-mortem delay in curing produced pieces which lost more nitrogenous material in soaking than the other lots; but the post-mortem period did not influence the limed-weight gain in contrast to McLaughlin's observation (22) that post-mortem storage decreased the ability of uncured hide corium to swell in lime. After deliming, all lots were subjected to vege-

table tannage and then evaluated by chemical and physical examination of the leather produced. The leather yield, thickness, specific gravity, chemical composition, and tensile strength and stretch were unaltered by the post-mortem period. However, the pieces subjected to the 72-hour post-mortem delay in curing produced leather with a spotted grain, and the leather was more permeable to water and to air than that from the pieces subjected to cure immediately or after a 24-hour delay.

Dempsey and Robertson (8) have reported upon two works-scale experiments relating the effects of post-mortem changes to the sole leather–making potential of the hides. In the first experiment 54 fresh English market hides of a weight suitable for sole leather were split down the backbone; one half of each was placed into tannery process immediately; the alternate halves of the same hides were staled for from 3 to 14 days before placing them into tannery operation. In the second experiment fresh and staled hides were salted and stored for periods of 1 and 6 months before placing them into tannery work. The leather produced was subjected to tannery evaluation and to microscopic assessment, chemical and physical examination, and practical wear tests by the British Leather Manufacturers' Research Association Laboratories. Staling periods up to 14 days caused no loss in sole leather quality as judged by the physical tests and practical wearing trials; up to 7 days of staling caused little difference in the weight of leather produced, although the leather weight loss was significant after 14 days of staling. Loss of hide substance due to staling seemed to increase the porosity of the leather, as indicated by lower apparent density and increased water absorption. Of course, grain damage was evident on the staled sides; 22 of the staled bends in the second experiment showed grain damage in contrast to no grain damage in the 30 alternate sides processed immediately after flaying. The cellular epidermal tissues suffer more severely from bacterial attack than do the leather-making fibers of the hide. Finally it was noted that the salted hides did not deteriorate excessively as a result of staling prior to curing; in fact, the staled hides subjected to salting tended to give better leather than similar staled sides placed into tannery processes without curing.

Haines (12) has studied brined-and-salted calfskin held in the cured state for two months, observing the putrefaction which occurred after it was soaked back to remove the curing salt. These soaked pieces were held at 37°C. for 0, 1, 2, 4, 8, and 16 days before further tannery processing, including sulfide liming, unhairing, deliming, pickling, chrome tannage, and fat-liquoring. Haines microscopically observed rapid degeneration of the cellular tissue, and especially the sebaceous glands and the fibroblasts, during the holding period after soaking, followed by deterioration of the elastic tissue; finally after 4 to 8 days there was loss of hide substance. Bacterial invasion from the flesh sides was observed as the holding period after soaking increased, with spore forms being visible in 48 hours and with very large numbers of

rod-shaped bacteria appearing as collagen degeneration became considerable. The fiber structure was opened up during the first day of the holding period, so that the final leather had improved fiber structure in comparison to the leather that was not held after the soaking back of the cured pieces. However, as this holding period increased in length, fiber deterioration was progressive. The chief point of attack seemed to be the grain and the junction of the grain and the corium; eight days of holding the soaked half-skin caused the grain to peel from the corium.

Koppenhoefer and Somer (16) have observed that the volatile nitrogen content of steerhide and the free fatty acid content of the hide corium are influenced by the post-mortem period prior to a 30-day cure at 20°C. They found that post-mortem periods of 1 to 2 days at 20°C. and 100% relative humidity have very minor influence on either of the mentioned analytical values but that these values increase rapidly with longer post-mortem times prior to curing.

Common salt is the usual agent used to arrest this post-mortem deterioration of skins and hides; its use alone and in combination with many additives has been the subject of numerous articles mentioned by Hausam (13,14). One reason for these studies on the use of additives to sodium chloride in curing is the desire to improve its curing efficiency. Secondly, the mandatory use of additives in nontaxed, inedible commercial salt in certain countries has required study of impure salts to separate the permissible from the unacceptable additives.

The preservative action of sodium chloride is at least partially dependent upon its dehydrating action. However, Rockwell and Ebertz (31) observed that the ability of salts to dehydrate tissue does not define their ability to control microbiological growth, citing especially the low antiseptic action of the very strongly dehydrating Epsom salt. Different sodium salts were found to differ in antiseptic value, with the chloride being much more efficient than the bromide. The low solubility of oxygen in sodium chloride solutions and their ability to retain carbon dioxide increase their antiseptic action. Since sodium chloride decreased bacterial liquefaction of proteins at much lower concentrations than those at which it could control the growth of microorganisms, it was suggested that interference with bacteriological proteolytic activity is one mechanism for the preservative action of common salt.

The inefficiency of sodium chloride as a preservative salt for hide curing is observed in phenomena such as "red heat" and "salt stains". The first of these, observed as pink to brick-red discolorations of the flesh side of the hide, apparently is caused by chromogenic, halophilic microorganisms. "Salt stains", observed by Bergmann (4) as rough, hard, contracted areas on the grain surface of the leather, show (under the microscope) gelled fibers and eroded areas in the skin tissue. At least as early as 1929 Bergmann, in a lecture to the International Council of Tanners, had reported on the isolation

from areas of red heat of chromogenic microorganisms capable of liquefying gelatin and on the isolation of colorless gelatin-liquefying organisms from "salt-stained" hides. Further, he observed that the organisms were tolerant to at least 8% NaCl in their growth media.

Bergmann (4) also reported on the practical evaluation, obtained through the cooperation of Carl Freundenberg G. m. b. H., of the resultant quality of leather produced from 4000 kilograms of red heat–discolored calfskins; particularly he reported upon the microbiological flora of these skins. These red discolored salted skins were found to lose more skin substance during soaking than well cured skins do; further, the discolored skins absorb more tanning materials, dyes, and lubricants during tannery processing. Motley-colored leather resulting from irregular finishing was noted with the poorly preserved skins. Bergmann's work showed that soda additions to the curing salt decreased the ability of the red-heat organisms to grow in the presence of sodium chloride; Mr. Walter Freudenberg attested to the practical value of soda additions in curing salt. Later work (14), however, has cast doubt on this.

Deficiencies in the preservative ability of common salt, manifesting themselves as red heat, salt stains, or hair slip, have continued to occupy the attention of leather chemists over the past quarter of the century, as the reviews by Hausam (13,14) and by Anderson (3) have indicated. Anderson's work is especially interesting; he isolated 80 strains of organisms from washings of hides and skins, finding over one quarter of them able to liquify gelatin. Sarcinae, Micrococci, and Staphylococci were the most salt-tolerant and were able to cause hair slip and to secrete a lipase, but they were unable to damage the hide fibers. Further, inoculation of sterilized hide with a lipase-producing strain gave a "stained" area in the hide resistant to vegetable tannin which was attributed to the reaction of the released free fatty acids and the lime. The Bacilli isolated were less salt-tolerant, but they were able to grow in the presence of salt and to hydrolyze the hide fibers.

Anderson (2) earlier had found a very salt-tolerant strain of *Bacillus subtilis* on salted sheepskins in the wool and heating in the pile. This strain was able to grow in 25% NaCl, while other strains he isolated could grow only in solutions with less than 12% NaCl. He was able to transform the salt-tolerance characteristics of the two strains by appropriate bacteriological techniques, making the salt-tolerant strain become sensitive to salt and vice versa. Thus, adaption of this common proteolytic Bacillus to salt is clearly shown, attesting to the correctness of the condemnation by McLaughlin, *et al.* (25) of the reuse of salt in skin and hide preservation. Since strains of Bacilli have been found to elaborate a collagenase (9), it might be informative to examine some of the salt-tolerant bacteria isolated from poorly preserved cured hides for strains specifically able to degrade collagen.

More recently fluorides, especially the silocofluorides, have been recommended as additives to curing salt (14). Kritzinger (17) has been particularly

active in the evaluation of silicofluorides, and his tannery-scale evaluation has indicated that the

"best curing, i.e., preservation of the valuable collagen, can be achieved by using about 50 per cent salt on the hide weight, the salt containing about 2 per cent sodium fluosilicate, storing the hides about 10 days. This cure would give low shrinkage values, in other words the tanner would buy relatively less hide substance. It is, however, a matter for agreement between the tanner and the curer and does not concern the efficiency of preventing bacterial damage to the stock. Perhaps a cure which would satisfy both curers and tanners without decreasing its efficiency would be to use about 50 per cent salt, mixed with sodium fluosilicate, and storing the hides for 30 days."

Anderson (2) presents data showing the ability of fluorides to control bacterial growth on hides. Kritzinger (see Hausam, 14) also has found that dipping or spraying the hides with fluosilicate solutions before salting is effective in the control of red heat and of beetle attack on hides. These techniques eliminate the problems arising from nonuniform blends of salt and fluosilicates in the dry state.

Many other additives to common salt have been suggested. Many salt impurities have been found which can cause alteration of the leather-making potential of hides. This extensive literature will not be reviewed here in view of Hausam's reviews (13,14).

Since green-salting of hides requires the formation of salt brine by solution of the salt in the hide moisture, it is logical to consider the possibility of brine curing. McLaughlin and Theis (23) have reported upon works-scale evaluation of brining versus green-salting, using an experimental plan in which alternate left and right sides went into each type of cure. The green-salted sides were salted with new salt within one hour after flaying. The sides to be brined were washed in running water and then brined for 24 hours in 25% sodium chloride solution, removed and drained briefly, and then salted down with new salt. The two packs were left in stacks for 6 to 8 weeks. The tannery processing was the normal process in the particular tannery and was identical for both packs. The evaluation of the results secured from these practical experiments indicated the following:

(a) Properly brined and tanned sides produce more leather from the same initial blood weight than equivalent sides that are not brined.

(b) Brined sides produce thicker and firmer leather with a minimum of stains.

(c) Brining offers a means of standardizing curing, but the process must be intelligently executed.

(d) Brined hides require special beamhouse treatment.

This curing procedure was somewhat similar to the Frigorifico cure of hides, which has had a good reputation. The success of these practical experiments and the good characteristics of such hides led to routine commercialization of the process.

DeBeukelaer (6) has reported upon the works-scale evaluation of this brining process. In his experiment advantage was not taken of the increased evaluatory sensitivity which can be gained from splitting the hides to two symmetrical sides for assignment to the two cures to be evaluated. Every other hide as it came to the packer's trimming table was placed in one or the other alternate cure pack. Green-salting, using a mixture of No. 1 and No. 2 rock salt (in part reused) at a level of 1 pound of salt per pound of green hide, was the first cure procedure. This pack of 500 hides was left in pile for five weeks. The alternate procedure was a brine curing, employing a saturated NaCl solution containing a neutral borax-boric acid mixture. Brining was continued for 14 to 20 hours in continuously saturated brine; agitation was continuous during hide addition and intermittent during the remainder of the brining period. The 500 brined hides were removed, drained for 30 minutes, and then placed into packs for 5 weeks, without the use of additional salt. These comparative packs were placed in the hide cellar in late July, and it is indicated that at the prevailing cellar conditions the brined hides could be stored for long periods without fear of deterioration.

The conclusions drawn from their experiment were:

(a) Heavy Colorado brined hides presented no difficulties in the usual beamhouse processing; since they were cleaner, they allowed shorter washing periods and reduction of the soaking period.

(b) The brine-cured hides led to higher white-weight gains.

(c) The brined hides gave a leather yield at least equivalent to the green salt-cured hides when converted into finders-type sole leather; a higher proportion of the bends, shoulders, and bellies from the brined hides were of heavier weight.

(d) Salt stains were characteristically absent from brine-cured hides.

Recent progress in brining has been particularly concerned with the mechanization of handling. Nordholm (28) has described one apparatus for this purpose, using constantly saturated brine with 1% hypochlorite. Strandine (36) and more recently DeBeukelaer (7) have described a commercial brining unit. Brining for twenty-four hours in constantly restrengthened and intermittently purified saturated brine (containing small amounts of antiseptics, e.g., NaOCl or Na_2SiF_6), followed by draining and then piling in packs for one month yields well cured hides with the desired shrink.

Strandine, DeBeukelaer, and Werner (37) have secured data on the stratigraphic distribution of sodium chloride and water in the flayed steerhide and in brined steerhide, while Kritzinger and van Zyl (19) have secured data

on the stratigraphic distribution of salt and water as a result of green-salting. There is a striking similarity in the exchange of moisture by salt in the two studies. Further, the different layers of the hides show significant differences in moisture and salt. Brining leads to the optimum uptake of salt and consequent dehydration after 24 hours, with longer periods of brining leading to less satisfactory dehydration. With green-salting, salt uptake continues for 48 hours, but the dehydration of the hide protein changes very little after 24 hours.

Kritzinger (17,18) has carried out works-scale experiments on the effect of cure and of storage time after cure on the quality of green-salted hides. These two articles offer evidence for the value of silicofluoride as an auxiliary to common salt. The second article is particularly valuable for the data which it contains on the influence of the time the hide is in the cure pack and in storage on the amount of the hide total nitrogen which is found to be extractible volatile nitrogen (0.12 to 0.17% of the total hide nitrogen); however, the packs cured with salt alone showed increased volatile nitrogen as the time in the cure pack increased. The salt level reported is 32.8% of the hide moisture, a level which is essentially independent of cure time, storage time, or the presence or absence of silicofluoride. The moisture level is about equivalent to the average value reported by Lollar and O'Flaherty (20) on American commercially cured packs. The volatile nitrogen content of salt-cured packs (after seven weeks of storage) increased from 0.28% for the pack held in the curing pack pile for only three days prior to storage to 0.58% for the pack held in cure pack pile for 30 days prior to the seven weeks of storage. Despite this the limed-hide weight yield expressed on the green-salted weight did not change. Further, the packs salted without silicofluoride showed only 1% lower limed-weight yield than packs cured with salt containing silicofluoride which showed the very low levels of volatile nitrogen. The tanner who converted these hides into leather, mainly vegetable-tanned, regarded all the hides as being well preserved and found that all the leather produced was very satisfactory. The significance of this interesting article will be discussed further later in this paper.

It is unfortunate that Kritzinger's articles do not record the ambient temperatures during the curing and the storage of the hides. Koppenhoefer and Somer (16) observed that as the ambient temperature during hide curing and storage was increased from 10° to 20° and to 30°C., the free fatty acid content of the hide corium and the volatile nitrogen content of the hide increased much more rapidly at the higher temperature as the time of storage increased. Thus, a 30-day period at 30°C. was more severe than a 90-day period at either of the two lower temperatures. Further, at 30°C. the level of deterioration continued to increase steadily as the storage time increased, while at the two lower temperatures the deterioration increased much more slowly after the early days of curing.

Stuart and Frey (38) have shown the critical importance of moisture and salt content of the cured skin in the deterioration occurring at 30°C. When the skin composition was changed from 49.2% moisture and 13.9% salt to 53.2% moisture and 12.5% salt, the bacterial count, ammonia, nitrogen, and free carboxyl groups of the skin specimens increased many fold. Below 49.2% moisture, with the consequent higher salt content, protein stability as measured by the above analytical methods was essentially constant. The character of the microbiological growth was observed to change at the moisture levels where increased deterioration was observed. Chains of rod-shaped organisms and clumps of monilial-like fungal cells were seen at the higher levels of deterioration, while bacterial cells occurring individually or in occasional groups were observed normally. It would be desirable to repeat experiments of this type on intact hide rather than on small pieces such as Stuart and Frey used, especially if the variation in the distribution of the salt and moisture in the skins and their cross sections were taken into account. However, it seems to be agreed generally that hide moisture levels as high as 50% are excessive, with 40 to 45% being more desirable and reported as common in commercial practice (20).

Frey and Stuart (10) have reported on a cold-storage experiment with green-salted calfskins. Packer, 8 to 12 lb., No. 1 selection, unbranded calfskins were placed into a pack laid down in September-October, using all new vacuum-pan-granulated salt. During the following February the skins were taken out of pack and placed into cold storage. The total number of skins employed was 192, divided into four random lots of 48 skins each. Each skin was split down the backbone, so that each lot was divided into two sublots each containing the alternate halves of the same skins. The skins were stored at approximately 36°F. and 70% relative humidity for periods varying from one to five years in yearly intervals. The sublots permitted direct comparison of the effect of any additional year of storage on the quality of the leather, under conditions which permitted the bilateral symmetry of the skins to contribute to the sensitivity of the experiment. The alternate halves of each lot of skins were subjected to tannages one year apart, so that these sublots had undergone a difference of one year in storage in the cured condition. When the second sublot was to be evaluated in the tanned state, the first sublot of leather was returned to the leather sorter along with the current lot. Thus he could compare alternate sides of the same skin, in which the differences in leather quality observed, if any, would logically result either from the effect of the additional one year of storage of the cured skins in contrast to one year's storage of the leather or from the differences in the tannage resulting from the year's elapsed time between tannage. The experiment did not provide any estimate of this latter possibility, but all processing was done at the same tannery with efforts being made to maintain a constant tanning and finishing process. The leather produced was a semianiline-finished calfskin shoe upper leather.

The results of the experiment showed that these well cured, green-salted calfskins could be held in cold storage for at least 5 years without suffering significant deterioration in their leather-making potential. The discussion of the paper emphasized that these skins were well cured, using new salt only, so that inoculation of the skins with salt-tolerant organisms was minimum. It was further emphasized that the natural contamination of skins with microorganisms is variable and that cold-tolerant organisms are also known. Hence, these results should be looked upon as the result of fortunate coincidence of ideal conditions throughout, rather than a demonstration of the generality of the results under less than ideal conditions.

Whitmore, Downing, and Sherrard (41) have presented data on the leather yield from Frigorifico-cured hides stored for four months at 31°, 48°, 80°, and 97°F., with and without added preservatives or resalting. The striking result of this experiment was the drastic decrease in leather yield after storage of the hides at 97°F.; this decreased hide quality was also indicated by a marked increase in the water-soluble hide protein in the cured hides. A 14% brine solution containing 1 part of sodium silicofluoride per 100 parts of salt was found to be able to retain the original low level of water-soluble hide substance in the Frigorifico hides as well as to retain most of the potential leather yield of the hides despite the storage for four months at 97°F.

Pal and Sarker (30) observed that well salted hides are not immune to deterioration even though salting follows immediately after flaying. The deterioration was followed by the determination of the soluble hide substance; this method was suggested as a measure of putrefaction. Their hides dried out during the four-month storage period so that the final moisture content was only 39.5%. Despite this fact the dry-basis hide substance fell from 96 to 71%, while the water-soluble hide substance increased over fourfold to 1.8% during the storage period. Hair slip was observed in one month, and red heat and slime were heavy at the end of the storage period. It appears probable that this deterioration was accelerated by unsatisfactory ambient climatic conditions in this experiment.

The several experimental and semi-works experiments discussed indicate certain of the conditions which must be considered for satisfactory preservation of green-salted hides. First, it should be kept in mind that common salt at best possesses only limited ability to conserve hide quality. Factors such as a post-mortem delay before salting, use of insufficient or dirty salt, use of salt of the wrong crystal size, curing excessively dirty, manure-covered, or fatty hides, are all factors which can contribute to a substandard cure. Further, it should be emphasized very strongly that improper handling of cured hides (such as exposure to temperatures in excess of 80°F. or to water or humidities sufficient to bring about 50% or more water in the cured hide) is a factor which favors accelerated deterioration regardless of the quality of the cure itself. Finally, it must be realized that hides are never sterile,

and that among the wide variety of organisms found are some which seem to possess particular ability to damage even salt-cured hides. It seems probable that inadequate or borderline curing conditions compounded with improper hide storage or shipment can interact to accelerate deterioration so that the hide fibers themselves deteriorate. There is considerable evidence that common salt can be made more efficient by additive agents, with sodium silicofluoride being one of the better agents for this purpose.

INDICATORS OF CURED HIDE QUALITY

Since the quality of cured hides is so variable, it is not surprising that tanners have developed specifications to define properly cured hides. The Tanners' Hide Bureau has issued "Standard Practice Governing Take-up and Delivery of Domestic Packer Hides, Revised Edition, 1955", and the Calf Leather Division of the Tanners' Council of America has issued "Standard Practices Governing the Take-up and Delivery of Domestic Packer, City and Collector Calf and Kip Skins". These standards are concerned with the weight and trim or pattern of the skin or hide, and the presence or absence of such hide defects as butcher cuts, scores, grubs, and warts. These are major factors in the determination of the grade of the skins or hides, which influences their market value; they are not directly concerned with curing. However, the hide standards state that hair-slipped hides are not deliverable unless the buyer and seller mutually agree. Excessive manure or fat and meat, which can interfere with a good cure, are compensated for by an allowance or by removal. The calfskin standards contain a statement with regard to quality of cure, which requires the use of evaporated new salt, G.A. size preferred, and which requires that the skins "should be fully cured in accordance with good commercial practice." General observance of these standards by the packer, broker, and tanner can do and has done much to standardize the commercial aspects of the transfer of the skins and hides from the seller to the buyer.

These standards are not very explicit in their definition of good cure; this may be the result of the fact that little information is available to define the quality of cured skins and hides, especially in terms of objective impersonal criteria that are generally acceptable. While the leather chemist has been active in other areas of the leather industry's quality control problems, such as the chemical and physical examination of leather, he has not devoted much attention to the development of hide-quality indices. Some criteria have been suggested, but these have generally not been subjected to sufficient evaluation under commercial conditions to determine their practical value.

Two articles published early in 1942 reported on the works-scale evaluation of two suggested criteria of the quality of cured hides. Somer (33) compared the sole leather yields and the volatile nitrogen content of samples taken

from the hides from which the leather was made. Based upon 44 lots of hides tested, "a figure of 74 per cent finished leather yield seems fair, and a volatile nitrogen content above 3 per cent would indicate poor curing". This article evidently contains a decimal error (20), and the reported values for volatile nitrogen are too high by a factor of 10. Whitmore, Downing, and Sherrard (41) found that the soluble nitrogen levels in ordinary, well cured Frigorifico hides increase with storage, from about 2 to over 5% expressed as hide substance. They felt that soluble nitrogen in cured hides which exceeds 5% when calculated as hide substance indicates hide deterioration. Variations of these two ideas have guided most recent studies of curing, such as those of Kritzinger (18), who employed both criteria.

These criteria have a logical basis, since they indicate that some changes are taking place in the protein components of the hides, including the hide fibers from which the tanner must produce leather. However, both of these indicators suffer from certain disadvantages. Volatile nitrogen can be lost during exposure of the hides, so that the residual amount found at any given time does not necessarily reflect the total deterioration that has occurred. It was mentioned in the discussion of Somer's paper that drying out of the hides would be expected to cause loss of volatile nitrogen. Further, both the volatile nitrogen and the soluble nitrogen in stored cured hides can arise from proteins other than the hide fibers; deterioration of the collagenous fibrous systems is not necessarily indicated when these indicators have increased in value. It may be that the greatest value of these indicators is their ability to serve as an "early warning" of conditions which will permit fiber deterioration, without any assumption as to the correlation between the amount of volatile or soluble nitrogen found in the hides and their leather-making potential.

Koppenhoefer and Somer (16) also found that the hide corium free fatty acid content increased in a parallel fashion to the increase in volatile nitrogen when hide pieces were subjected to adverse curing and storage conditions. The method requires more elaborate sample preparation and laboratory manipulations than the volatile nitrogen method; perhaps it is for this reason that it has received little or no practical use. However, Anderson (3) observed that an invasion of salt-cured hides by salt-tolerant organisms causing hair slip involves lipase-secreting organisms, and that these organisms preceded the large rod-shaped organisms which were found to be proteolytic. This might suggest that increase in the corium free fatty acids could serve as a valuable early warning indication of potential deterioration of the hide fibers. Anderson further observed that these lipase-secreting organisms can be made to simulate the tanning-resistant "raw spots" sometimes met in vegetable tanning practice. These facts suggest that the corium free fatty acids might be a valuable criterion of the quality of cured hides, but this possiblilty has received little commercial evaluation.

Microscopic examination of thin sections cut from hides suspected of deterioration during curing or storage can also furnish evidence on the leather-making potential of the hides. Hides exhibiting slipped grain will show areas in the cross-sections where the grain, or epidermal tissue, is lifted away from the remainder of the hide, and the boundary area between the grain and the hide beneath may be "chewed away", or severely depleted by the growth of microorganisms. The invasion of the hide fibers by the microorganisms can be demonstrated by staining the sections; the pattern of invasion reported by Anderson (3) is very typical. Deteriorated cured hides also show under microscopic examination that the cellular tissue, including the fibroblasts, has been destroyed. This microscopic method of examination has particular value, since it gives an indication of the particular area of the hide cross-section in which the deterioration is occurring. It suffers from the problem inherent in all micromethods, either chemical or microscopic, that adequate sampling becomes very difficult. Its use is very desirable in the examination of specific hide areas which exhibit other evidence of deterioration, but the amount of work required would be prohibitive in any attempt to use this method as a quality control survey tool to estimate the quality of all lots of hides received at the tannery cellar.

O'Flaherty (29) introduced an additional concept into the question of estimation of the leather-making potential of cured skins or hides in his article entitled "What Really Makes Leather". He notes that a 60-pound cured hide may contain only 20 pounds of leather-making material and that the actual value of the cured hide would be more correct if based on its content of leather-making material than on its green-salted weight. This concept does not imply that criteria of cure quality reflecting the presence or absence of deterioration changes are not valuable; it adds the consideration that, even with the best quality of cure and storage, profitable leather making cannot be anticipated unless the tanner secures the actual leather-making protein at an economically feasible price. O'Flaherty therefore proposed that skin or hide lots received by the tanner should be subjected to analysis to determine the content of leather-making substance.

During the past two years we have had an opportunity to secure some information on the significance of some of these possible indicators of the leather-making potential of cured hides. This work is summarized at this time to stimulate further thinking so that valid indicators of the quality of cured hides will become available and their correlation with the leather-making potential of the hide lots will be known. This seems particularly desirable since the American Leather Chemists' Association has now appointed a raw stock evaluation committee (40).

SAMPLING OF CURED HIDES

Sources of variability in cured hides are all too well known in the industry and include differences due to breed and sex; differences resulting from cli-

matic and nutritional conditions during the animal's life; damages from disease, insect attack, and physical agents such as barbed wire, thorns, and brands; and the changes due to improper practices during curing and storage. There is very little information available on the magnitude of this variability from area to area in a given hide and from hide to hide in a given lot. Yet any analytical method to estimate the leather-making potential of a lot of hides arriving at a tannery cellar would have to utilize some adequate sampling method to minimize the effect of this variability on the value of the results secured from examination of the sample.

Tancous (39) and Deasy (5) have presented some information on the variation from area to area and from side to side on salted and on brined steerhides. Tancous' data covered both halves of 4 steerhides, with sampling of eight areas within each side. She presented data on the original sides before curing and on the opposite sides after one half was salt-cured and the alternate half was brine-cured. Deasy reported on the composition of ten different experimentally brine-cured steerhides, based upon 21 different sampling areas per side; individual analyses were performed on each of the 210 specimens. This study was modelled after that of Mandel and Mann (26), who developed a rational solution of the problem of selecting the best sampling location to reflect the side average for any particular property of the leather under consideration. Deasy deduced that the preferred sampling location for brined steerhides would be an area adjacent to the backbone and located 20 to 28 inches forward from the root of the tail. Additional data are presented on the variability from hide to hide in this preferred sampling location for two different lots of commercial brine-cured hides. Hide composition factors for which data are given in her paper include the content in the cured hide of moisture, ash, total nitrogen, and hydroxyproline. Since supplemental information secured on these hide specimens indicated that the cure and storage conditions prior to analysis were ideal, this article presents information on the minimum expected variability with brine-cured hides. It must be realized that nonideal conditions during curing and storage of the hides can only increase the within-hide and between-hide variability; therefore, conclusions based upon the data secured by Tancous and Deasy must minimize the estimate of the variability to be expected in commercially cured hides. It is therefore very difficult to assess the significance of data similar to those reported by Lollar and O'Flaherty (20) on commercially cured hide lots.

Since so little information is available on the usual variation to be expected in commercially cured skins and hides, it was decided to use the procedure developed by Deasy (5) for sampling, examining each of the sides individually for its composition in the sampling area. Further, few data are available on the effect of the cure and storage conditions of the hides on their physical properties and the nature of the correlation between the hide composition

and these physical properties. However, it would seem that the potential fibrous properties of the leather would be more dependent on the physical properties of the hide fibers than on chemical properties of the hides. It was therefore decided to secure information on the physical properties of the hide specimens taken from the sampling area recommended by Deasy.

EXPERIMENTAL METHODS USED

The hide evaluatory tools employed included examination of the hide inspector's report, determination of the hide volatile nitrogen and its content of leather-making substance, microscopic examination of cross-sections of the cured hide specimens, and determination of the strength of the cured hide specimens. Somer's volatile nitrogen procedure (33) was modified by using a direct distillation of the volatile nitrogen in the hide extracts, using calcium hydroxide as the alkalinizing agent; this procedure was shown to give results equivalent to Somer's more tedious procedure. The Neuman and Logan hydroxyproline assay (27) was used for the determination of the leather-making substance of the hide specimens. The other chemical analyses performed involved customary laboratory procedures. The fat content was obtained by chloroform liquid-liquid extraction of a hide hydrolyzate (6N H_2SO_4 for 16 hr.), since direct Soxhlet extraction of the hide specimens did not remove all the fatty material. The physical tests performed on the specimens taken from the hides in the location specified by Deasy (5) were made in the same manner as on leather. The cured hide specimens were tested as received, with the curing salt and water present in these hides being a diluent of the protein fibers during testing. Microscopic examination of the cross-sections of the hides included inspection to detect loosening of the epidermis, depleted areas under the epidermis, disappearance of the fibroblasts or of the grain grease, and fiber gelling.

Evaluatory tools employed on the leather included the leather sorter's grading of the leather, the yield, the chemical composition, physical characteristics, and cross-sectional character as determined by microscopic examination. The sampling position used in the latter determination was that suggested in the American Leather Chemists' Association method J 1 (1), in which the test area *W*, to the rear of the kidney area of the side, is recommended for physical test specimens on light leather. This sampling location gave us a leather sample for both chemical and physical testing which was located to the rear of the hide sampling area. The appropriate methods for the chemical analysis and physical testing of leather given in either the Association's methods (1) or in Federal Specification KK-L-311 were employed.

The data in this paper were secured from four different lots of leather and from the hides from which the leather was produced; code letters *NE*, *DE*, *NC*, and *DC* have been used to designate the four lots of hides and the leather made therefrom. *NE* designated the sides that were subjected to the

normal salt-curing procedure in an experimental pack immediately after flaying; *DE* designated the alternate halves of the same hides laid down in an experimental pack after a 48-hour delay. *NC* designated hides given an immediate normal commercial salt curing, while *DC* designated hides given a commercial salt curing following a reported overnight post-mortem delay prior to curing.

The hides and the leather designated as *NC* have been reported upon in detail by Lollar and Wilson (21); an elk-type chrome-tanned side leather was produced in the tannery from well cured and preserved small packer hides. The *DC* hides and leather were sampled through the courtesy of a west coast tannery that was experiencing difficulty in leather quality which was attributed to the poor quality of the hides resulting from delay in curing. A certain fraction of the leather produced was reported to have a very low tearing strength; on these sides the corium fibers were spongy and the flesh side had a porous appearance.

The leather produced from these *DC*, or delayed-cure, hides was chrome-tanned; being designed for use as a baseball glove leather, it was softer and had less temper than the elk side leather in the *NC* lot. The tanner who produced this *DC* leather reported that he employed an 18-hour soak at 50° to 60°F., followed by green fleshing. The unhairing procedure involved hair destruction in 48 hours at 70° to 75°F., followed by scudding. The tannage was an integrated bate-pickle-tan procedure, employing calcium formate in the pickle and a prepared sugar-reduced chrome liquor. The tanned leather was wrung, set out, split and shaved, and then colored orange. The colored leather was fatliquored with a commercial sulfated oil with low cold-test characteristics, set out, and toggle-dried with temperature and humidity control. The dried leather was sammied, staked, and graded and measured. In comparison with the leather in the *NC* lot, this lot of leather was secured from a dissimilar beamhouse operation, but the tannage and lubrication were similar in principle. Of course, this leather was finished dissimilarly and was softer than the *NC* leather. Any comparisons between the two leathers would involve all these tannage differences in addition to the hide difference; therefore it was considered desirable to supplement the results secured on these commercial leathers with results secured under experimental conditions designed to minimize the differences other than the hide curing difference.

The leather designated *NE* and *DE* was made from 50 native steerhides from a kosher kill, selected at the packing house trimming table as the hides came down from the killing floor; the hide selection was designed to yield 50 pounds cured weights. These 50 hides were cut down the backbone, and alternate halves were placed into one of two cure packs, with 25 right and 25 left sides in each pack. The pack designated *NE* was immediately salted down with new No. 1 salt. The pack designated *DE* was made up from the sides which had been thrown into a pile while the heat was still in the sides, without

the initial addition of any salt. After a two-day staling period at 65°–70°F., the staled sides were removed from the pile and placed into a cure pack, using reused salt entirely. The two packs were built up under the instruction of the cellar foreman as separate small packs 50 sides high, folding the skirtings over so as to maintain the customary level pack surface. The completed packs with the respective salts between the sides were then edged with salt and allowed to lie undisturbed for the normal 30-day cure at 65°–70°F.

The two experimental packs of sides were taken up by the hide broker's inspector who was taking up the regular packs in the cellar at the same time. The pack which was cured immediately after flaying (*NE*) showed a shrinkage of 18.8%, while the delayed-cure pack (*DE*) showed a shrinkage of 19.6%. The inspector's records showed nothing to indicate any significant difference between the two experimental packs or between the experimental packs and the commercial packs taken up at the same time. No hair slip was noted on any of the 100 sides, although a few sides in each of the experimental packs seemed to have slightly loose hair in spots. The sides from both experimental packs were graded and bundled by the cellar workmen and shipped to the cooperating tannery by truck during a normal late fall day in the Cincinnati area. These hides were held for four weeks in the tannery hide cellar, which was cool because of the prevailing weather.

The 100 sides in this experiment had been coded when they were cut, to preserve the original hide identity throughout the curing and storage period. When the tanner was ready to soak these sides, they were sampled to secure the cured hide specimens and coded to preserve the original hide identity throughout the tannery processing of the sides. All 100 sides were made up into a single lot for processing in the tannery and were brought back together again at intervals during the process for inspection and to insure that all the 100 sides were being processed similarly. When the sides were available as finished elk-type shoe upper leather, they were measured and graded by the tannery personnel and sampled to secure the leather specimens for laboratory evaluation of the experiment.

The tannery which processed these 100 sides employed a 14-hour still soak followed by a 7-day, hair-recovery, lime-sulfide unhairing procedure with still vats in which the hides are reeled forward each day. The sides were then unhaired, lime-fleshed, and bated for 1 hour at 90°–95°F. with tryptic-type enzymatic bate. The bated sides were then pickled overnight in a paddle, using 8% NaCl and 1.5% H_2SO_4. Chrome tannage in a drum was followed by splitting and shaving. The grain splits which we evaluated in our work were retanned with chrome and then given a light vegetable retannage or topping. After fatliquoring and coloring, the sides were set out and then paste-dried. The paste was washed off the dried leather, which was then staked, plated, grain-buffed, and finished as brown elk-type shoe upper leather. This process, of course, differs both in the beamhouse operation and

in the tannage from the conditions used on the previous two lots, so that any comparison between the leather properties of the *NC* and the *DC* leather with the *NE* and *DE* leather would involve some process differences as well as the hide differences. However, the comparison between the *NE* and *DE* packs involves only the difference in cure, since the experimental design took advantage of the bilateral symmetry of hides, and since the sides from the two different cure conditions were subjected to identical commercial tannery processing. Hence, these latter sides should furnish sensitive indications of the effect of the delayed cure on the quality of the cured hides and the quality of the resultant leather. The results from the *NC* and *DC* packs of leather and their hides are presented because they confirm the results secured from our experimental packs; however the results in these commercially cured packs subjected to the dissimilar tannages prompted us to lay down our experimental packs. All the leather and hide data have been presented in tables and figures comparing all four packs, but the differences in hides and tannery conditions must be taken into account in interpreting the results secured.

TABLE I

CHARACTERISTICS OF THE CURED HIDES USED

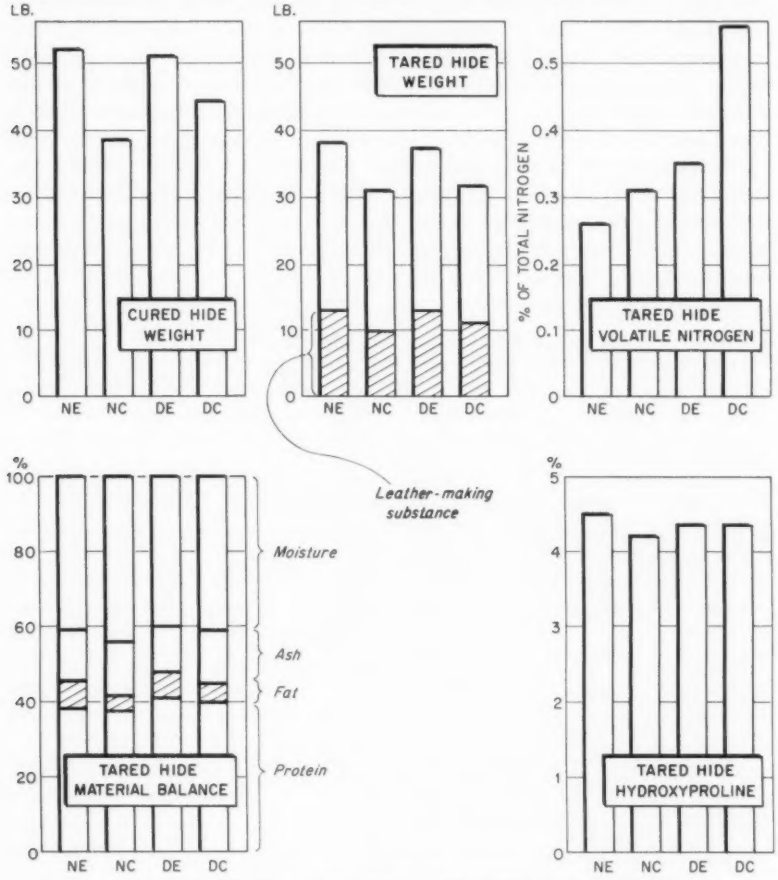
Hide Lot Average Characteristics	Normal Cure Experimental (NE)	Normal Cure Commercial (NC)	Delayed Cure Experimental (DE)	Delayed Cure Commercial (DC)
Cured-Hide Weight, lb.				
As received basis	52	38	51	44
Tared basis—fleshed and hair-clipped	39	31	38	32
Hide Composition—Tared Basis, %				
Moisture—wt. loss at 80°C. in vacuum	40.9	44.2	40.2	40.9
Ash—residue at 600°C.	13.8	14.7	14.0	14.7
Fat—$CHCl_3$-soluble	5.9	2.8	6.5	3.3
Protein—% N x 5.62	39.3	38.0	40.4	40.2
	99.9	99.7	101.1	99.1
High-Quality Indices				
Hide inspection rating	O.K.	O.K.	O.K.	Poor
Histological rating*	12	13	11	10
Volatile nitrogen—% of total N	0.27	0.31	0.35	0.56
Leather-making substance, lb.**	12.9	10.0	12.4	10.4
Hide Physical Properties—Tared-Hide Basis				
Thickness, mils	204	168	204	178
Ball puncture, lb.	162	170	156	171
Tongue tear, lb.	80	60	79	61
Notch tear, lb.	143	—	138	117
Tensile strength, lb.	394	—	385	—
Stitch tear, lb.	—	125	—	143

*A score, varying from 16 for a well cured hide to 6 for a poorly cured hide, resulting from microscopic examination of hide cross-sections.

**Lb. leather-making substance = tared-hide weight x % hydroxyproline x 7.5.

EXPERIMENTAL RESULTS

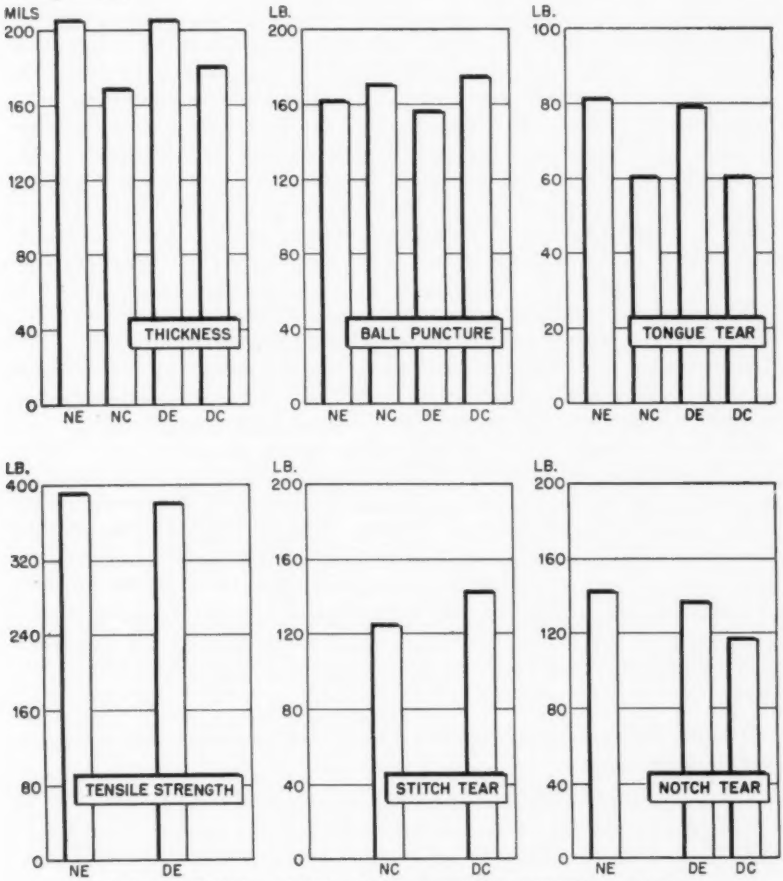
Table 1 and Figures 1 and 2 present data secured on the characteristics of the hides. Because of the steerhides available when the packs were laid down, our experimental packs yielded cured hides which were heavier than those included in the commercial packs. The specimens from all packs were hair-clipped and fleshed to yield an estimate of the tared weight of the hides which



NE — NORMAL SALT CURE — EXPERIMENTAL PACK.
NC — NORMAL SALT CURE — COMMERCIAL PACK.
DE — DELAYED SALT CURE — EXPERIMENTAL PACK.
DC — DELAYED SALT CURE — COMMERCIAL PACK.

FIGURE 1.—Composition of the hides used.

the tanner would actually be able to use in his process. This hair clipping was done with the same clippers customarily used by tanners who make hair-on leather. The fleshing was done on a fixed-blade sole leather splitter while the hide specimens were in the fast-frozen state. Table 1 and Figure 1 show that the estimated average tared weight of all the hides considered in this work lay between 31 and 39 pounds, with our experimental packs representing the heavy hides.



NE—NORMAL SALT CURE—EXPERIMENTAL PACK.
NC—NORMAL SALT CURE—COMMERCIAL PACK.
DE—DELAYED SALT CURE—EXPERIMENTAL PACK.
DC—DELAYED SALT CURE—COMMERCIAL PACK.

FIGURE 2.—Physical properties of hides used.

Table I and Figure 1 show that the four lots of hides differ significantly in their volatile nitrogen content. The hides from the delayed commercial cure, code *DC*, show a volatile nitrogen content of 0.56% of the total hide nitrogen. This is one of the higher levels of volatile nitrogen which we have observed in our sampling of commercially cured hides (20). Further, our experimentally cured pack of sides subjected to immediate salt curing, code *NE*, has 0.27% of volatile nitrogen which is the lowest for the four packs. The level of volatile nitrogen secured indicates that a very good cure was secured on both the *NE* and *NC* lots of hides, which were cured immediately. The relatively low level of volatile nitrogen secured on the sides from the delayed experimental cure, code *DE*, was somewhat surprising; however, this may reflect the temperature at which this experiment was performed. Since this work was done it has been possible to confirm this result; another lot of hides held for 72 hours at about this temperature before a special brine cure has also shown low levels of volatile nitrogen in the cured hides. Since a twofold variation in the volatile nitrogen content of the four lots of hides was secured, it seemed possible that differences in the leather quality could be observed.

The tared hide specimens were analyzed to determine their composition, with particular reference to the content of leather-making substance. Table I and Figure 1 show that the total of the moisture (weight loss at 80° C. in vacuum), ash or salt (residue weight at 600°C), chloroform-soluble fat, and protein (Kjeldahl nitrogen times 5.62) is close to 100%, as it should be. The analyses for the four lots of hides are fairly similar except for the lot coded *NC*, which was more moist and hence contained less protein even though it also contained the least fat. Further, the hides from lot *NC* contained the least amount of hydroxyproline. This lot of hides, which was initially the lightest in weight, contained the least protein and hydroxyproline, so that it contained the least amount of leather-making substance of all the four lots. A possible significance of this fact will be indicated later. It should be emphasized that the delayed cures did not decrease the content of leather-making substance in the hides, even in our very sensitive split-hide experiment.

The differences in the chemical composition of the four lots of hides may thus be summarized.

(*a*) A significant difference exists in the volatile nitrogen content of the hide lots, with the hides from the *DC* lot showing the most, followed by the *DE* lot, the *NC* lot, and the *NE* lot in order. The level of the volatile nitrogen on the latter two lots is judged to be indicative of good curing practice.

(*b*) The heavier hides used in the experimental lots have resulted in a higher level of leather-making substance for lots *NE* and *DE* compared with lots *NC* and *DC*.

Table I and Figure 2 present data on the physical properties of the hides used in the experiments. The thickness of the tared hides reflects their weight as would be expected. Thus, the hides from the experimental cures were significantly thicker than those of the commercial experiments. Also, the hides from lot *NC* were the lightest in weight and the thinnest of the four lots. However, within the individual lots the correlation between the thickness and the load to rupture the hide specimens was not statistically significant for the tests run. Considering the effect of the delay in curing on the physical properties of the hides, it will be noted that the effect is very slight. Even the experimental lots, where the additional sensitivity resulting from the split-hide experiment could be used advantageously, did not demonstrate a statistically significant decrease in the hide strength. Microscopic examination of the cross-section of the hides confirmed this observation. Though the sides subjected to the delayed cures, and especially those from the commercially delayed cure, showed loss of fibroblasts and some deterioration in the grain area, the fibers themselves were altered only to a small extent. Hence, it does not seem surprising that the physical properties of the hide specimens have not been significantly affected by the delayed cure, since hide physical properties must be the result of hide fiber properties.

TABLE II

CHARACTERISTICS OF THE LEATHER PRODUCED

Leather Average Characteristics	Normal Experimental (NE)	Normal Commercial (NC)	Delayed Experimental (DE)	Delayed Commercial (DC)
Tanners' Evaluation of Leather				
Yield, ft. per lb. hide	0.80	0.89	0.77	—
Quality—% C grade or better	65.3	64.8	65.3	*
Chemical Composition of Leather				
Moisture—% wt. loss at 100°C.	15.1	13.0	14.9	11.3
Excess ash—% total ash minus % Cr_2O_3	2.2	2.6	2.2	1.6
Fat—% $CHCl_3$ solubles	7.5	6.3	7.4	13.8
Chrome-tan salt—% Cr_2O_3 x 2.71	9.1	7.9	9.1	7.3
Protein—% N x 5.62	61.8	64.8	61.9	63.2
Residue—100 minus above 5 constituents	4.3	5.4	4.5	2.8
Chrome oxide—% Cr_2O_3 on H.S. basis	6.39	4.54	6.36	4.27
Physical Properties of Leather				
Thickness, mils	70	72	69	68
Ball puncture, lb.	57	39	57	68
Tongue tear, lb.	23	15	22	21
Notch tear, lb.	37	—	34	40
Stitch tear, lb.	74	56	70	80
Mullen grain crack, lb.	488	339	464	337
Mullen total burst, lb.	608	450	591	467

*Tanner reported an unknown fraction of "weak, easily torn leather".

Table II and Figure 3 present the properties of the leather produced by the tanneries from these hides. All of the leather was split to equivalent commercial weight of the grain portions; however, the leather from the *NC* lot was the thickest of the four lots. It will be recalled that the hides in lot *NC* were the lightest in weight and the thinnest of the four lots. Hence a greater proportion of the original weight of the hides must have gone into the grain

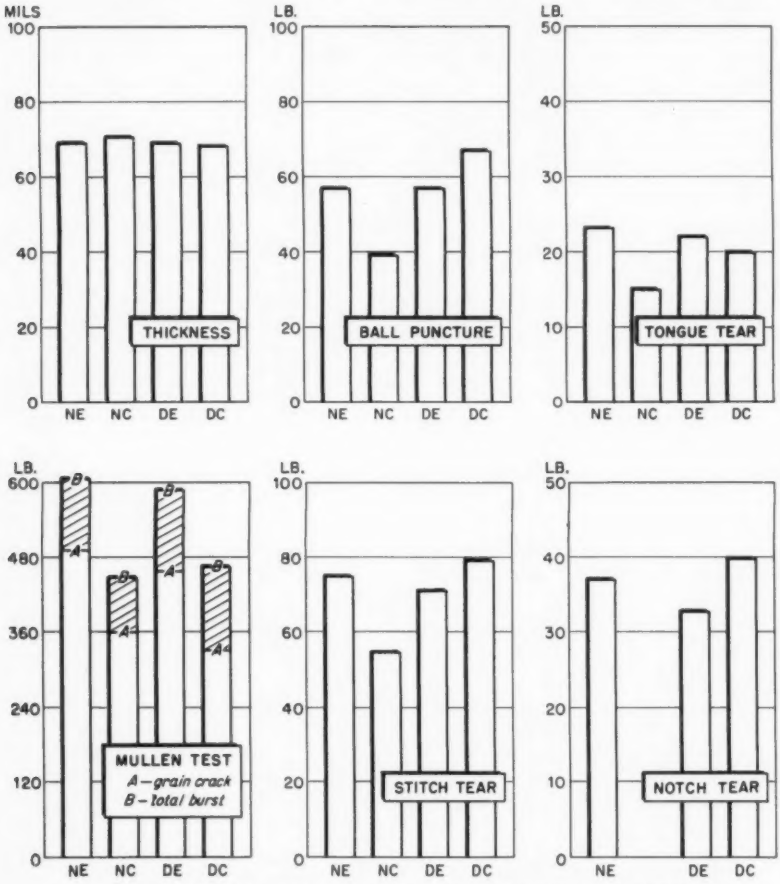


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FIGURE 3.—Physical properties of the leathers.

portions of the leather considered here than in the other three lots. Similarly, the yield of leather from the *NC* lots of hide was the highest for the three lots where the tanner reported his yield figures to us. It will be noted later that this leather from the *NC* lot is also the weakest in spite of the slightly greater thickness of the *NC* leather specimens.

Tannery grading evaluation of the quality of the leather was of course biased by possible differences in the evaluatory criteria used in the three tanneries involved. However, the average quality of all the leather produced from these lots of skins was identical insofar as examination of the tannery reports could disclose, except for the complaint from the tannery which processed the *NC* lot of hides that a fraction of the leather was weak and easily torn. However, this did not manifest itself in the particular hides sampled for our examination. The comparison of the effect of the delayed cure with the regular cure on our experimental packs could take advantage of the sensitivity of paired sides to detect differences. Despite this fact the tannery inspector was unable to detect a significant difference in the leather quality assignable to the delay in cure. The sides from the same hides were presented to the inspector in coded pairs. He was requested to express a preference for one or the other side and to evaluate both for general character, especially break and grade. While there was some possibility that the leather from lot *DE* was somewhat more mushy than that from lot *NE*, the difference was not significant in the matched-pair presentation. Further, examination of the finished leather and of the stock during the several stages of the tannery processing showed that the sides were all at least equal in quality to the regular production sides going through the tannery at the same time. All the leather produced in this experiment was sold in normal commercial channels after due allowance for loss in value caused by sampling.

The physcial properties of the leather from the four lots of hides are given in Table II and Figure 3. The breaking load values, except for ball puncture and Mullen grain crack and total burst, were secured on our Instron Tester. Though the individual thickness of every specimen tested was determined, the values are presented as the average load in pounds to break the specimens, since it will be shown later that the assumption of linear dependence of the breaking load on thickness is not justified. The data secured were analyzed by appropriate statistical procedures, including the analysis of covariance (32) to correct for any possible contribution of leather thickness to its strength, and the conclusions given below are based upon the statistical analyses of the data.

Over-all comparison of the strengths of the leathers from the four lots of hides is biased by the effects due to the different hides used in the experiment and the different tannery procedures used. However, it will be noted that the leathers are of similar chemical composition. Lot *DC*, designed to be much softer than the other leathers, contains significantly more fat.

The leathers produced from the commercially cured hide lots *NC* and *DC* contain only about two-thirds as much chromic oxide on the hide-substance basis as do the leathers produced from our experimentally cured lots *NE* and *DE*. Otherwise the composition of the leathers is very similar and reveals no effects assignable to the delay in cure. Hence a general comparison of the physical properties of the leathers seems feasible.

Certainly the leather produced has not decreased in strength as the volatile nitrogen content of the original hides increased. This is true of the comparison between the four lots, as well as for the hides within the *DC* lot of hides where the greatest range of volatile nitrogen content was observed. It is interesting, however, that the leather from the *NC* hides (which hides showed the lightest weight, least thickness, and least leather-making substance) is the weakest leather. Beyond this no over-all difference in the strength of the leather is discernible, and certainly there is no striking effect of the delay in cure on the leather strength.

The experimental evaluation of the effect of the delay in cure was planned to take advantage of the increased experimental sensitivity of the paired-side experimental plan. The data in Table II will show that the leather from the experimental delayed-cure pack, coded *DE*, is slightly weaker in several of the physical properties than the regular-cure matched pack, coded *NE*. Statistical examination of the data secured showed that this was of doubtful significance. Certainly this difference in leather strength is of no practical significance, and the leather from the *DE* pack of hides shows better physical properties than the leather coded *NC*, which is a commercially acceptable good-quality shoe upper leather. Hence, the physical examination of these leathers has confirmed the inability of the tannery inspection to detect practically significant differences in the leather which could be assigned to the delay in the cure of the hides.

SIGNIFICANCE OF THE RESULTS SECURED

Approximately 200 sides of leather produced in normal commercial tannery operations have been evaluated; half of these sides originated from hides given immediate, efficient salt-curing and the other half from sides cured only after a post-mortem period has elapsed. One hundred of the sides came from 50 hides split along the backbone immediately after flaying, and separated into two equivalent, paired-side packs. One pack was immediately salt-cured, while the equivalent alternate pack was cured after being held 48 hours at 70°F. Despite the sensitivity of this experimental plan it merely confirmed the earlier observation from the commercial packs that the delay in curing was not reflected in the leather quality. It is therefore necessary to consider the significance of these results.

These results are similar to those reported by Frey and Stuart (11), who found little difference in leather quality between lots of calfskin which had

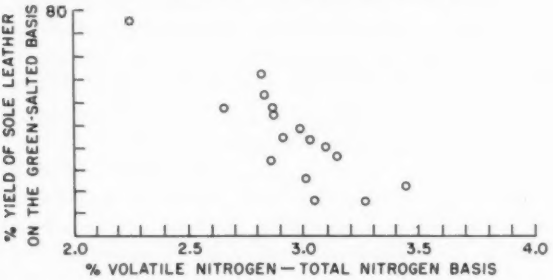
obviously deteriorated in quality due to poor curing, in comparison with the alternate sides of the same skins which had been well preserved. The same question which they raised in the discussion of their results must be raised with regard to the data reported here. The results in this paper, coupled with those secured by Frey and Stuart and those reported in the introduction to this paper, indicate that a level of deterioration in the quality of the cured skins or hides that is readily recognized does not always indicate that differences in the quality of the leather will be detected. This fact emphasizes again that indicators of hide cure quality may be "early warning indicators" of unsatisfactory curing and storage factors but may not indicate a direct correlation with the leather-making potential of the lot of hides.

It is certainly logical that there is a level of hide deterioration, unknown though it is, which is sufficient to be reflected in the quality of the leather. The essential difficulty in the proof of this statement, and in the establishment of acceptable specifications for good-quality cured hides, is the lack of any standardized measures of cured-hide quality. The best standardized indicators are the level of volatile nitrogen in the hides and microscopic assessment. It has been pointed out that there is a twofold variation in the volatile nitrogen of the hides represented in this work. The levels of volatile nitrogen found on both of the delayed-cure lots of hides are in excess of 0.3%, which is the critical level found by Somer (33 and 20) for hides going into sole leather tannage. The delayed-cured hides showed histologically demonstrable damage. Hence, some deterioration did occur in these hides during the post-mortem period. One can therefore only conclude that the extent of damage was insufficient to override the effect of all the other factors which establish the properties of the finished leather. It might therefore be informative to consider individually some of the reasons why the leather has been so insensitive in reflecting the known differences in the cure quality of the hides.

The volatile nitrogen figure as an indicator of cured-hide quality rests primarily on the work of Somer (33), Koppenhoefer and Somer (16), and Kritzinger (18). Figure 4 presents a summation of information taken from these sources. It is obvious that the amount of volatile nitrogen to be found in cured hides is a function of the ambient temperature during cure and storage, as well as the post-mortem period before cure. In view of the low ambient temperatures in our controlled delayed-cure experiment, both during post-mortem storage and curing and during storage of the bundled hides, it is logical to assume that our level of volatile nitrogen should be low. In comparison, the commercial delayed-cure hides were processed under warmer climatic conditions and no doubt were exposed to a higher average ambient temperature. Hence, the higher level of volatile nitrogen in these hides seems logical. Despite this, however, the hides did not produce the poor-quality leather that the level of volatile nitrogen would suggest.

The data secured by Kritzinger (18) may be particularly informative in this regard. These data are summarized on the right-hand side of Figure 4. Kritzinger's observations suggest that, regardless of the time hides were left in cure pack, the volatile nitrogen content increased with the time that the hides were stored; further, that the shorter times in cure pack led to lower

FROM SOMER—*JALCA*, **37**, 34 (1942).



FROM KOPPENHOEFER AND SOMER—*JALCA*, **34**, 34 (1939).

FROM SOMER—*JALCA*, **37**, 34 (1942).

FROM KRITZINGER—*JALCA*, **49**, 99 (1954).

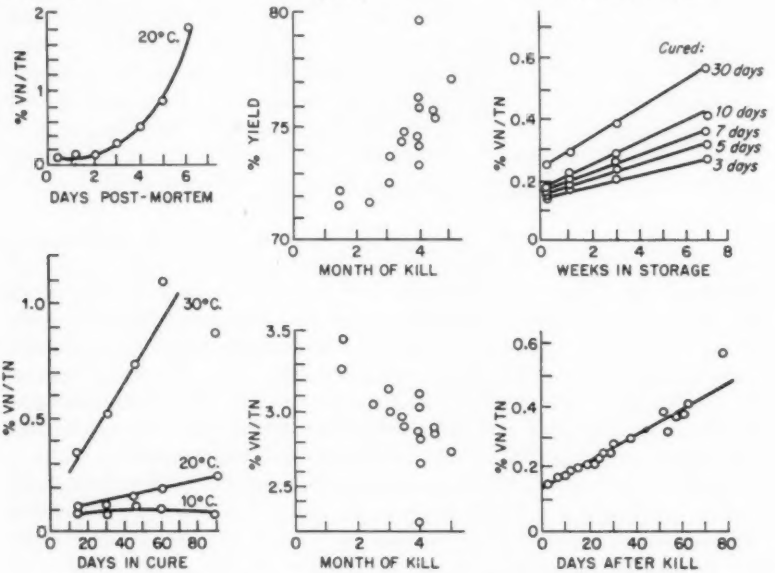


FIGURE 4.—Some aspects of the volatile nitrogen assay.

levels of volatile nitrogen in the hides. A possible significance to these seemingly anomolous results may be seen in the lower right-hand corner of Figure 4, where Kritzinger's data have been replotted to relate the hide volatile nitrogen content to the total time elapsed after flaying regardless of the period in cure or storage. It will be noticed that a linear relationship exists, suggesting that the volatile nitrogen content reflects a continuing deteriorative mechanism which takes place in the hides whether the hides are in cure pack or in bundle storage.

Examination of the data secured by Somer (33) suggests another characteristic of the volatile nitrogen content as an indicator of cured-hide quality. The yield of sole leather is known to be related to the season of kill, in part because of the effect of such factors as hair length and manure on the quality and amount of leather-making substance in a lot of hides. Also, there is a seasonal influence in the response of hides to tannery processing due to differences in tannery variables. Somer's data show a direct linear dependence between the month of kill and the yield of sole leather produced and an inverse linear dependence between the volatile nitrogen content and the month of kill. Since yield and volatile nitrogen are both serially correlated with the month of kill, it would be informative to consider possible causes of the serial correlation which could be the basic factor causing the lower yield of leather. At this late date it is impossible to do this with precision. However, it may be that the observation made by Kritzinger is involved. If all the hides went through the tannery at approximately the same time, then the time between flaying and tannage must have varied from pack to pack. If the packs went through the tannery at a fixed time after flaying, then tannery seasonal responses may have influenced the results.

Finally, it must be suggested that sole leather weight yields may reflect the deteriorative changes from which increased levels of volatile nitrogen arise more sensitively than do the side leather quality indicators used in this work. Volatile nitrogen increase in cured hides seems to be a complex phenomenon reflecting such factors as the time and ambient temperature between the time of flaying and the time of testing. Our experiments on the post-mortem effect were carried out over periods of up to 48 hours at 20°C., followed by holding the cured sides for periods of time up to two to three months before conversion of the sides into leather. Our volatile nitrogen figures lie mostly in the region between 0.25 and 0.6% of the total nitrogen and are consistent with the characteristics discussed in the literature for the volatile nitrogen assay, particularly with the observations of Kritzinger (18). Since these levels of volatile nitrogen did not reflect themselves in marked decreases in the quality of side leather, one might conclude that the volatile nitrogen indicator of cured-hide quality may be more sensitive to deteriorative changes which affect sole leather yield than to types of changes which affect the quality of the side leather. In this regard one should recall that

microscopic evidence of a marked influence on the fibers of these hides due to the delayed cure was not secured. The observed changes in the cellular tissues of the hides would not be expected to influence side leather quality. Only a limited number of the specimens of the *DC* (commercial delayed-cured) hides showed significant gelation of the hide fibers. Hence, it does not seem surprising that the properties of the side leather were satisfactory on all the sides included in this work.

There are variations in the physical properties of the leather produced. Since these variations do not seem to reflect the quality of the cure within the limits of these experiments, one must consider the possible cause of the differences.

It is customary to regard the thickness of the leather as a significant factor in the strength of the leather. In extreme ranges this would be expected to be true. However, within the small variations of thickness represented by commercially equivalent leather weights, one would not expect the large strength variations found in finished leather to be due to thickness variations alone. It seems more logical to assume that the strength of the final leather is a reflection of its fibers and their mechanical properties. Hence, the data secured were examined to see whether such factors as the strength of the hide fibers in the cured state, the thickness of the leather, the protein content of the leather, and its fat content, influence the strength of the leather. In general the results secured show that the content of protein within a given specimen is the most significant factor which controls the strength of the leather.

The method used to secure this information was the examination of the correlation coefficients (32). Since each hide and the leather made from it had been coded to preserve identity throughout all the experimental work, and since specimens from each of the hides and the leather made from them had been examined individually, it was possible to calculate correlation coefficients involving the within-lot variations in hide and leather properties. Table III shows the data thus secured on the resistance of the leathers to puncture by a ball-pointed plunger ⅛ inch in diameter, while Table IV shows similar data for the conventional two-hole stitch-tear strength. It must be recalled that the square of the correlation coefficient (r) may be taken as some measure of the degree of common relationship between the two variables concerned. For the size of experiments involved in this work the correlation coefficient (r) for a significant level of 1% is about 0.35, which indicates a common relationship of only about 12%. Hence, correlation coefficients below this magnitude are certainly without any practical significance.

It is obvious from both Tables III and IV that the protein content of the leather is the most significant factor considered. As the levels of chrome-tanning salt and of fat increase, the leather strength decreases as shown by

TABLE III

CORRELATION COEFFICIENTS FOR BALL PUNCTURE TEST OF LEATHER WITH BALL PUNCTURE TEST OF HIDE, AND WITH LEATHER CHARACTERISTICS

(Within-lot Variations)

Code	Hide Puncture	Leather			
		Thickness (Mils)	Protein %	Fat %	Cr_2O_3 %
NE	+0.34	———	+0.22	+0.01	−0.38
NC	+0.35	+0.29	+0.59	−0.43	+0.24
DE	+0.01	———	+0.46	−0.03	−0.29
DC	+0.21	+0.65	+0.71	−0.75	−0.03

r for significance at 0.01 level — 0.35.

TABLE IV

CORRELATION COEFFICIENTS FOR STITCH TEAR TEST OF LEATHER WITH STITCH TEAR TEST OF HIDE, AND WITH LEATHER CHARACTERISTICS.

(Within-lot Variations)

Code	Hide Tear	Leather			
		Thickness (Mils)	Protein %	Fat %	Cr_2O_3 %
NE	———	−0.19	+0.40	−0.13	−0.28
NC	+0.20	+0.31	+0.49	−0.31	+0.10
DE	———	+0.02	+0.39	+0.02	−0.25
DC	+0.21	+0.55	+0.70	−0.68	−0.02

r for significance at 0.01 level — 0.35.

the negative correlation values. In other words, the dilution of the hide fibers by either chrome-tanning salt or fat does not contribute to increased leather strength. While the correlations between hide strength and leather strength, and between leather thickness and its strength, are generally positive, they are not generally large enough to have practical significance.

It seems pertinent that the weakest leather of the four lots was that in lot *NC*. This lot was made from the lightest, thinnest hides, with the least content of leather-making substance. In view of the dependence of the strength of the leather on the leather protein and in view of the characteristics of the leather made from the *NC* hides in comparison with other leather made from poorer hides, it seems worthwhile to re-emphasize O'Flaherty's

suggestion (29) that the tanner should be more concerned about the amount of leather-making substance in the hides he purchases. In a later paper information will be published concerning this method of evaluation of the quality of cured hides.

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REFERENCES

1. ALCA Method J-1, Provisonal Method, 1953.
2. Anderson, H. *J. Soc. Leather Trades' Chemists*, **29**, 215 (1945).
3. ———. *Ibid.*, **33**, 250 (1949).
4. Bergmann, M. *J. Intern. Soc. Leather Trades' Chemists*, **13**, 599 (1929).
5. Deasy, C. *JALCA*, **51**, 271 (1956).
6. DeBeukelaer, F. L. *JALCA*, **33**, 470 (1938).
7. ———. *Chemistry and Technology of Leather*, ed. F. O'Flaherty, W. T. Roddy, and R. M. Lollar. Reinhold Publishing Corp., A. C. S. Monograph No. 134, 1956, Vol. 1, pp. 201–7.
8. Dempsey, M., and M. E. Robertson. Reported by M. E. Robertson, *Progress in Leather Science* (London: British Leather Manufacturers' Research Association, 1948) pp. 104–5.
9. Evans, D. F., and A. G. Wardlaw, *J. Gen. Microbiol.*, **8**, 471 (1953); *C. A.*, **47**, 8184c.
10. Frey, R. W., and L. S. Stuart. *JALCA*, **36**, 650 (1941).
11. ——— — ———. *JALCA*, **31**, 254 (1936).
12. Haines, B. M. *J. Soc. Leather Trades' Chemists*, **37**, 363 (1953).
13. Hausam, W. *Collegium* **814**, 55 (1938). Translated into English, *J. Intern. Soc. Leather Trades' Chemists*, **23**, 44 (1939).
14. ———. *Das. Leder*, **1**, 18, 47, and 69 (1950). Translated into English by Fox, S. E. *J. Soc. Leather Trades' Chemists*, **35**, 142 (1951).
15. Kaye, Madge. *J. Soc. Chem. Ind.*, **48**, 141T (1929); taken from D. J. Lloyd, *British Leather Manufacturers' Research Association Seventh Annual Report*, 1927, Part III, p. 77.
16. Koppenhoefer, R. M., and G. L. Somer. *JALCA*, **34**, 34 (1939).
17. Kritzinger, C. C. *JALCA*, **46**, 445 (1951).
18. ———. *JALCA*, **49**, 99 (1954).
19. ——— and H. M. Van Zyl. *JALCA*, **49**, 91 (1954).
20. Lollar, R. M., and F. O'Flaherty. *Leather Mfr.*, **72**, No. 2, 8 (1955).

21. ——— and C. D. Wilson. *JALCA*, **51**, 206 (1956).
22. McLaughlin, G. D. *JALCA*, **36**, 435 (1921).
23. ——— and E. R. Theis. *JALCA*, **17**, 399 (1922).
24. ——— — ———. *JALCA*, **17**, 377 (1922).
25. ———, I. H. Blank, and G. E. Rockwell. *JALCA*, **23**, 300 (1928).
26. Mandel, G., and C. W. Mann. *J. Research Nat. Bur. Standards*, **46**, 99 (1951).
27. Neuman, R. E., and M. A. Logan. *J. Biol. Chem.*, **184**, 299 (1950).
28. Nordholm, N. D. *Hide and Leather and Shoes*, **114**, No. 11, 16 (1947); *JALCA*, **43**, 262 (1948).
29. O'Flaherty, F. *Leather and Shoes*, September 3, 1949.
30. Pal, B. N., and P. K. Sarkar. *Tanner* (India), **6**, No. 10, 15 (1952); *JALCA*, **48**, 304–5 (1953).
31. Rockwell, G. E., and E. G. Ebertz. *J. Infectious Diseases*, **35**, 573 (1924).
32. Snedecor, G. W. *Statistical Methods* (4th ed.), Ames, Iowa: Iowa State College Press, 1946.
33. Somer, G. L. *JALCA*, **37**, 34 (1942).
34. Stather, F., and H. Sluyter. *Ledertech. Rundschau*, **25**, 85 (1933); *JALCA*, **30**, 134–35 (1935).
35. ——— and H. Herfeld. *Collegium*, **792**, 215 (1936).
36. Strandine, E. J. *Das Leder*, **2**, 220 (1951).
37. ———, F. L. DeBeukelaer, and G. A. Werner. *JALCA*, **46**, 19 (1951).
38. Stuart, L. S., and R. W. Frey. *JALCA*, **33**, 198 (1938).
39. Tancous, J. J. *JALCA*, **50**, 278 (1955).
40. Thorstensen, E. B. *JALCA*, **50**, 582 (1955).
41. Whitmore, L. M., G. V. Downing, and S. S. Sherrard. *JALCA*, **37**, 41 (1942).

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DISCUSSION

MR. A. G. FLEISCH (Pfister & Vogel Tanning Co.): Gradually it seems we are carrying away some of the superstitions that have existed for many years in our industry, and it has seemed in the last several years that the rate of tearing these superstitions apart is increasing quite rapidly. With work of this type we will soon come down to knowing what we are doing in our industry.

All I can say right now is that we certainly appreciate it. We all have had the opportunity in our own tanneries, whenever we have seen something wrong, to say, "Poor cure." I hope our hide buyers don't hear about this, because we won't have that excuse in the future.

DR. WM. R. COX (Seton Leather Co.): Do you feel there is any possibility that perhaps with a longer time in storage you might mask some of the effect of poor initial curing practices, such as delayed cure?

DR. LOLLAR: Yes, I think that is a possibility. Certainly it seems to me that what is going on in the cure and in the beamhouse is one continuous process of degradation, change, and ultimate removal of the noncollagenous portion of the hide. There have been other experiments performed which suggest

that if you do not bring about some of these changes in the cure or in the storage, you are going to have to bring them about in the beamhouse. I suspect that the differences would have been other than those that we secured if we had done the work at a different temperature. I feel confident of that. It might well have been that we would have gotten a different result if the hides had been converted into leather immediately at the end of the 30-day cure period. But we have no information on that.

DR. COX: There seems to be a correlation in Somer's work between yield and volatile nitrogen. Do you believe that the volatile nitrogen actually correlates with yield, or that the breakdown products of noncollagenous proteins might become volatile through storage?

DR. LOLLAR: In all our work we have found the most characteristic thing that is happening to the hides is that during adverse cure and storage conditions the noncollagenous material is being removed. The collagen fibers themselves seem to be very resistant to deterioration. This does not minimize the problems that would come up from grain stains and so forth. I would again like to emphasize that if you do not have the characteristic long, rod-shaped organisms on the hide fibers, it is our experience from microscopic examination that you do not seem to have hide fiber damages. I therefore suspect the volatile nitrogen factor may be reflecting something that is not concerned with the leather fiber.

DR. COX: It won't correlate with yield?

DR. LOLLAR: It may correlate; we do know what factors influence yield. It may be that the strength of the fiber won't be damaged, but the ability of the fiber to take on the tanning material will be affected. Therefore, particularly in sole leather, the yield you can get might be changed even though the fiber is not actually weakened. Its reactivity may be changed. I think we are going to have to look into this work which Somer reported earlier and understand it better.

DR. COX: Those yield figures of Somer have the long-hair factor in them, and other factors which should not, I would think, be affected by volatile nitrogen. I do not see how they should correlate with yield.

DR. LOLLAR: I have thought of that, and I think it is a valid point. I also wonder—and the information does not seem available at this time—as to whether the decreased volatile nitrogen in relationship to the month of kill might reflect that the animals killed in May might be converted into leather sooner than those killed in January, so that there was less chance for the globular or nonfibrous proteins to deteriorate. Maybe that is the reason the volatile nitrogen went down. Manure might be another factor, also.

DR. BUECHLER: I would like to ask if any observations were made by tannery personnel on these two packs of leather as they went through the tannery. We see here that apparently little difference was found in the final leather. Was there any difference in the processing? For example, did they unhair at the same rate?

DR. LOLLAR: We examined them repeatedly throughout the process—not only Mr. Hauck and myself but also the tannery personnel. In no case could we note anything that would distinguish any of these sides from any other sides going through the tannery, unless it was the fact that they were consistently better than the average going through the tannery. Our sort figures would support this. Our yield figures, corrected for the fact that we were cutting out quite a bit of area in our sampling, would support the conclusion that they were as good as, if not better than, the average in the tannery. And there was no difference by any test that was significant between the alternate sides.

DR. STUBBINGS: I am certainly happy to see these results reported. The literature shows that there was one other experiment done of this general type, where they actually assessed the final leather qualities in terms of the cure that had been given the hide. That was done by a government agency back about 1936. They found no difference in the final leather qualities either, with some tremendously horrible cure conditions. We could not, in several curing experiments that we ran within our group about four or five years ago, find any real difference in the leather. We have always been hesitant about these results because the tanner feels that if he has anything like hair slip, he has a bad proposition on his hands. And yet from your results and ours it seems that the leather always turns out all right. My only comment is that maybe we are just looking at factors that do not really affect leather when we talk about cure, or they might affect the leather in terms of weight.

DR. LOLLAR: Our delayed-cured sides did have slightly lower yields, but it seems as though our difference was borderline in nature.

LEATHER SCHOLARSHIPS

A number of scholarships are available to leather engineering students at Lowell Technological Institute. Scholarships are offered by the Commonwealth of Massachusetts, the City of Lowell, the LTI Alumni Association, the Department of Leather Engineering (headed by Dr. Albert E. Chouinard, active ALCA member), the New England Tanners Club, and several industrial firms.

All scholarships are awarded by the Lowell Technological Institute Scholarship Committee. Application should be made to the Director of Admissions, Lowell Technological Institute, 1 Textile Avenue, Lowell, Massachusetts.

CREEP RUPTURE OF LEATHERS UNDER TENSILE LOADS*

DONALD H. RUSSELL**

The Franklin Institute
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ABSTRACT

Certain dumbbell-shaped tensile strength specimens of leathers show a type of creep rupture or static fatigue when subjected to static tensile loads close to their ultimate strength. Studies made at The Franklin Institute show that the static fatigue life of leather decreases as the load increases, and increases with leather thickness. Holding leathers under relatively low tension (static loads), especially in the minimum stretch direction, was found to produce increased static fatigue life, apparently due to fiber orientation.

INTRODUCTION

It is well established that the ultimate strength of a high polymer, for any given stress condition, is not merely a numerical value but rather is defined by the length of time of the stress application. Thus, it has been reported that for materials such as cellulose acetate fibers (1, 2) and cotton and nylon tire cords (3) there is not a sharp value for tensile strength; instead there is a varying rupture time which is a function of the applied tensile load. Actually, in the case of cotton tire cords an inverse linear relationship has been established between the static tensile breaking load and time to rupture (4, 5, 6). Also more recently there have been some excellent fundamental stress-strain studies of collagen and leather (7, 8, 9, 10).

In experiments at The Franklin Institute evidence was found that tensile strength specimens of fresh chrome-retan upper leather show behavior similar to the aforementioned creep rupture of fibers and cords. Consequently a program was carried out to investigate the phenomenon further. In a limited number of experiments (triplicate samples on 12 specimens)† we found that the static fatigue life of leather decreased as the applied static tensile stress was increased, and increased with the thickness of the leather. In a second investigation we found that the static fatigue life of leather can be greatly

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†Since we did not have the complete previous history of the leather specimens we have not included the experimental data.

increased if the leather is first aged or held under a static tensile load to cause fiber orientation.

EXPERIMENTAL PROCEDURE AND RESULTS

Dumbbell-shaped tensile strength specimens (ASTM D412-51T, Die D) were cut from pieces of fresh, fully finished, chrome-retan upper leather selected from the shoulder and butt areas of a single hide fresh from the tanners. The specimens, varying in thickness from 65 to 80 mils, were all cut from the leather in the direction which showed maximum stretch or elongation and stored for seven days at 72°F. and 42% relative humidity prior to testing. After storage the samples were clamped in a test fixture kept at the same temperature and humidity as above, and the load was applied by means of weights placed in a weight pan. Elongation was determined with a cathetometer by following the separation of ink lines marked on the narrow portion (5/16 *inch width*) of the sample. The test was continued until the sample broke, and the time to rupture (time after last increment of load was applied) was recorded as the static fatigue life. See Table I for typical results.

TABLE I

STATIC FATIGUE LIFE OF FIVE LEATHERS

Leather		Static Load		Time to Rupture
No.	Thickness* (mils)	(lb.)	(psi)	(minutes)
1	80	70	2800	345
1a	80	98	3900	152
2	65	50	2470	36.5
3	75	50	2130	300
3a	75	70	2980	168
4	75	70	2980	160
5	70	70	2980	128

*Method No. 1021 Federal Specification KK-L-311a

The experimental method may be stated briefly as follows: A load considerably below the immediate breaking load was applied, and the elongation was measured until no further change occurred over a 30-minute period. At this point elongation was considered to be essentially complete. The load was then increased slightly, and the elongation was again measured in the same manner as described above. This same procedure was repeated until, with the next load increment, elongation was continuous to the rupture of the specimen.

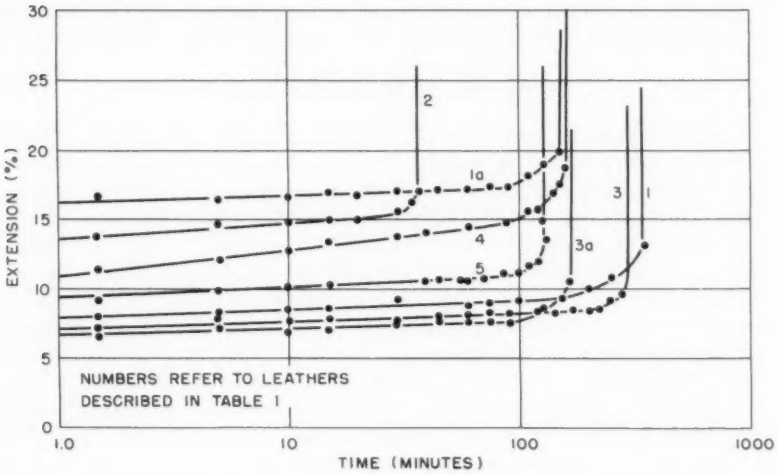

FIGURE 1.—Creep rupture curves for 5 leathers.

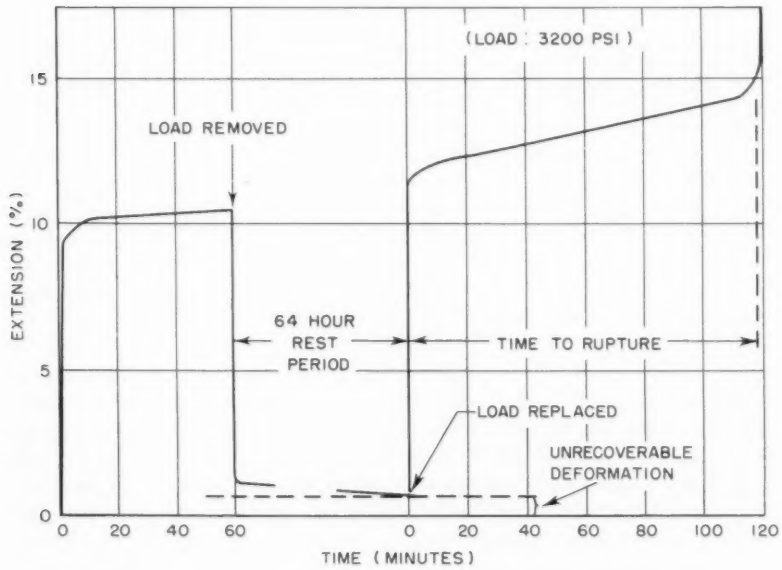

FIGURE 2.—Creep rupture curve for a prestretched leather.

The creep curves that were obtained (see Figure 1) are similar to those typical of viscoelastic materials; that is, there is first an instantaneous elastic deformation at the moment of loading followed by a relatively flat portion where the leather apparently elongates and the structure distorts slowly. The rate of elongation suddenly increases (slope is greater) just before the sample ruptures, indicating that major structural breakdown has started.

In one set of experiments the load (equivalent to 3200 psi with the sample dimensions given above) was removed from a sample after one hour, and the sample was allowed to relax for 64 hours, and then the sample was reloaded and permitted to elongate and rupture. The instantaneous elongation was essentially completely recovered as soon as the load was removed, but the permanent deformation was not recovered even after 64 hours. When the same load was reapplied, instantaneous elongation occurred again to about the same extent as in the first loading, and the sample then finally ruptured (see Figure 2).

TABLE II

EFFECT OF AGING UNDER STATIC LOADS

(*Leather Thickness*: 70 *mils*)

Sample	Stretch Direction	Days Aged at 1100 psi Static Load	Time to Rupture (minutes)	
			2300 psi	2970 psi
A	maximum	0	15	—
	"	3	875	—
	"	7	1080	—
	minimum	0	—	1515
	"	3	—	1575
	"	7	—	1515
B	maximum	0	10	—
	"	3	705	—
	"	7	900	—
	minimum	0	240	—
	"	3	568	—
	"	7	722	—

If leather (which is composed of folded polypeptide chains) is aged under a static tensile load, a fiber orientation or permanent set (probably at both the molecular and structural level) occurs. Generally, an oriented system shows higher strength than an unoriented system, and consequently leather should be stronger in the oriented direction after aging than before aging if the set is permanent. However, there is also a strong directional effect in

leather which gives it a maximum stretch direction and, perpendicular to it, a minimum stretch direction which also must be taken into account.

Table II shows that in the case of a leather aged for seven days under relatively low loads in the direction of maximum stretch large increases (seventy to eighty fold) in the times to rupture (under a higher final load, the value of which was determined experimentally) were effected. The increase after three days aging is about three-quarters that of the increase after seven days. The extent of improvement in static fatigue life appears to be relatively independent of the elongation in the maximum stretch direction. However, in the minimum stretch direction the increase in static fatigue life appears to be very dependent on the elongation of the sample.

CONCLUSIONS

Under low loads, which we have found actually to strengthen leather, the fibers become oriented so that more of them are aligned in the direction of load application. When higher loads are applied, causing creep rupture immediately or over a period of time, evidently the coherence of the leather structure is being decreased first by increasing the distance between the structural components and ultimately by breaking of bonds. Similar but much smaller changes in properties would be expected in the plane through the thickness, but they would depend greatly on the nature of the leather and would undoubtedly be of smaller order.

We can differentiate between initially rapid, recoverable elongation of an elastic sort due to orientation and later, much slower, irreversible creep of an apparent viscous nature. This irreversible creep apparently corresponds to permanent damage to the leather structure and ultimately results in failure.

REFERENCES

1. Haward, R. N. *Trans. Faraday Soc.*, **38**, 394 (1942).
2. ———. *Ibid.*, **39**, 267 (1943).
3. Busse, W. F., E. T. Lessig, D. L. Laughborough, and L. Larrick. *J. Appl. Physics*, **13**, 715 (1942).
4. Shorter, S. A. *J. Textile Inst.*, **15**, T207 (1924).
5. Pierce, F. T. *J. Textile Inst.*, **18**, T475 (1927).
6. Karrer, E., J. N. Grant, and R. S. Orr. *Textile Research J.*, **17**, 314 (1947).
7. Hall, R. H. *J. Soc. Leather Trades' Chemists*, **35**, 11 (1951).
8. Mitton, R. G., and E. F. Nattrass. *J. Soc. Leather Trades Chemists*, **34**, 299 (1950).
9. Grassmann, W. *Das Leder*, **1**, 57 (1950).
10. Kagi, *Textil Rdsch.*, **8**, 168, 233 (1953).

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LIFE LINES

Brief Biographies of Our Contributors

RAYMOND HAUCK received an A. B. in Chemistry from Miami (Ohio) University in 1950. He was employed during the next two years by the General Electric Company, A.G.T. Division, as a statistical analyst. Since December, 1952, he has been a research associate at the Tanners' Council Research Laboratory. He has been concerned since 1953 with problems dealing with the quality of cured hides, participating in work carried out at the Tanners' Laboratory under the sponsorship of the Tanners' Hide Bureau. In June, 1957, he received his M. S. degree in Leather Chemistry from the Graduate School of Arts and Science of the University of Cincinnati.

DR. ROBERT M. LOLLAR is Associate Professor in the Department of Tanning Research at the University of Cincinnati where he earned both M.S. and Ph.D. degrees. A member of the staff of the Tanners' Council Research Laboratory since 1941, he has honored the *Journal* with frequent contributions. He is also one of the *Journal's* regular abstracters. In 1954 he received the Alsop Award.

DONALD H. RUSSELL is a graduate of Temple University. He was employed as a Research Engineer by the Franklin Institute in the Colloids Section, Chemistry and Physics Division, from 1948 to 1957. In this capacity he worked on many problems for clients of the Institute. He is now employed by Reliance Steel Company, McKeesport, Pennsylvania.

DR. HAROLD G. TURLEY was born and educated in England. He has been associated with Rohm and Haas Co. for more than 30 years and now holds the title of Research Associate. His first contribution to the *Journal*, "A Chemico-Histological Study of Leather Manufacture", published in 1926, attracted immediate attention and was the first of many noteworthy papers. Dr. Turley, a past president of *ALCA*, received the Alsop Award in 1946. He is now president of the International Union of Leather Chemists' Societies.

ARNALDO N. ROSEIRA, author of "Paper Chromatographic Analysis of the Naphthenic Syntans" in last month's issue of the *Journal*, received his bachelor's degree in chemistry from the Pernambuco Catholic University. After experience in many tanneries and allied industries he joined the National Institute of Technology where he is now a member of the dyestuffs section. At present he is engaged in research on the electroforetic behavior of dyestuffs.

ALCA NEWS

Proceedings, Reports, Notices, and News

of the

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NOTICE TO AUTHORS AND ABSTRACTERS

The Editor-in-Chief expects to be out of the United States from about August 9 to October 10, 1957.

From July 15 to October 1 all manuscripts, copy for abstracts, and anything else for the Editor-in-Chief's attention should be mailed to:

Dr. T. C. Thorstensen
Associate Editor
Research Foundation
Lowell Technological Institute
Lowell, Massachusetts

OBITUARIES

Arthur Harvey, F.R.I.C., F.C.S

The International Union of Leather Chemists Societies has suffered a sad loss in the death of Mr. Harvey, the Honorary Secretary, on Saturday, April 27, 1957. It was due largely to Mr. Harvey's vision and efforts that the International Union was established in 1947. This was a project dear to his heart.

Mr. Harvey was a link with the past and was active in and knew very well the problems of running conferences with two international societies participating jointly. When, in the course of time, most countries formed their own national leather societies, Mr. Harvey realized that the time was ripe for a truly international union of the leather chemists societies of the world. Largely through the efforts of Mr. Harvey and his associates, the American Leather Chemists Association eventually participated in the affairs of the Union.

He was a charming and affable secretary, always with a ready smile and a helping hand. The smooth running of the past four conferences was facilitated by Mr. Harvey who laid the groundwork during the months preceding the meetings. We looked to him for advice and guidance which he gave freely. Right up to the day of his death Mr. Harvey was active with the correspondence in connection with the details of planning the Rome Meeting in September, 1957.

Besides his duties as Honorary Secretary to the International Union Mr. Harvey was editor and publisher of the *Journal of the Society of Leather Trades' Chemists*. He was also in private consulting practice for the leather industry in Great Britain.

Captain Raoul Berger

With deep regret we announce the death of Captain Raoul Berger, an associate member of this Association since 1949, who died for France at the head of his command at Djebel-Tanyout, Algeria, on August 3, 1956. Captain Berger had been awarded the Médaille Militaire and the Legion of Honor. At the request of Professor Chambard the next graduating class of the French Tanning School will be designated "Promotion Raoul Berger".

SECRETARY'S NOTICE

I am advised that due to the large number of papers submitted for presentation at the meeting of the International Union of Leather Chemists Societies it has become necessary to extend the meeting by one day, thus including Friday, September 20. Technical and scientific papers and their discussion will take place on Thursday and Friday, September 19 and 20.

FRED O'FLAHERTY
Secretary

THE COVER

This month's cover depicts the beautiful Milton Park Laboratory of the British Leather Manufacturers' Research Association. This Association, founded in 1920, is supported by contributions from 280 member firms supplemented by government grants. Its library on leather is considered the best in Great Britain. The staff of sixty—all with a background knowledge of tanning and the leather industry—includes specialists in chemistry, physics, microbiology, engineering, statistics, etc. Regular publications of the Association are the "Members' Journal" and "Monthly Digest." "Laboratory Reports," usually printed twice a year, give detailed accounts of research work carried on in the many well-equipped laboratories. Two publications have become standard works: "Progress in Leather Science, 1920–1945" and "The Chrome Tanning Process."

A vast new potential market has been opened up for bark—at present largely a waste material of the lumber, pulp, and paper industries. Armour Research Foundation scientists, in cooperation with Canadian Forest Products Ltd., have developed a method to convert bark into an inexpensive and effective soil builder.

In tests conducted with greenhouse plants and field crops the soil builder was found to be more effective in promoting growth and improving the soil than either peat moss or commercial soil conditioners.

Production of the soil builder involves grinding the bark and condensing the tannin by the addition of formaldehyde followed by acidification with hydrochloric or sulphuric acid. The mixture then is heated for a brief period to complete the condensation process. Water and other excess chemicals are removed and the material is washed and dried.

The soil builder does not fertilize the soil, as such. Rather, it increases the tilth of the soil; that is, it eliminates clods or hard lumps, enabling plants to feed better and grow. —*Frontier*, published by Armour Research Foundations, Spring, 1957.

ABSTRACTS

Microscopic Investigation of the So-called "Salt Stains." A. Küntzel and T. Stintz. *Bol. Asoc. Quim. Espan. Ind. Cuero*, **15**, 47–53 (1954).—The 3 different types of salt stains (flesh side, grain side, and internal), their influence in the tanning process, their origin, and the granulation of the fiber at the place of the stains, are studied, and about 25 photomicrographs are shown. The salt stains are not due to a bacterial growth but to the simultaneous action of 2 factors: (1) a postmortem decomposition of noncollagen materials of the conjunctive cellules, where the blood residues have an important role, and (2) the infiltration of soluble Ca and Mg salts. These can be insolubilized by a sufficient addition of Na_2CO_3. J.B.B. and M.G.B.

Raw Materials for Fiber Leathers for Slipper Soles. A. Suchomel and M. Mazanek. *Kozarstvi*, **6**, 193–94 (1956).—Fibers from Cr and vegetable-tanned leathers, in the ratio of 2 to 1, are mixed with chloroprene, coagulated with Al_2SO_4 at pH 5–6, and vulcanized. Accelerators used are ZnO, CaO, and MgO. A syntan (Binkotan), a condensation product of dihydroxydiphenyl sulfone, is used as a stabilizer. L.M.

Influence of Tannery Effluents on the Vah and Demanovka Rivers in Liptovsky Mikolas. Z. Nanackova-Zekeova. *Kozarstvi*, **6**, 197–200 (1956).—The annual input of Czechoslovak tanneries is about 40,000 tons of hides for vegetable, and 20,000 tons for Cr leather. This corresponds to about 3 million cu. m. of tannery effluent. The Liptovsky Mikolas tanneries produce 41 liters of effluent per kg. hide in vegetable tannage, and 65 liters per kg. in Cr tannage. The O_2 numbers, in grams per liter, for side upper leather wastes, fur dressing, and vegetable tannage, are 4.18, 0.84, and 2.1 respectively. The physicochemical changes in the receiving streams are described, including bacterial counts for various types of organisms above and below the city. L.M.

A Method for the Rapid Determination of Calcium in Pelt. A. Stehlik and M. Podolska. *Kozarstvi*, **6**, 162–63 (1957).—Calcium is determined colorimetrically with pyrogallolcarbonic acid, which produces a blue color. The determination is possible by using standards containing 0.2 to 1.0 mg. Ca in 10 ml. without using a photocolorimeter. Prisms 2 to 4 mm. square are cut from the pelt 5 cm. from the spine and 5 cm. from the root of the tail. A 2.0 ± 0.05 g. sample is hydrolyzed by boiling for 5 min. in 10 ml. of 0.1 *N* HCl. The hydrolyzate is mixed with 1 ml. of 2% starch solution, 1 ml. 2*N* NaOH, 1 ml. ether, and 10 ml. of a saturated solution of the reagent. The latter is made by boiling 10 g. pyrogallol for 2 hr. with 40 g. $NaHCO_3$ and 70 ml. water, under reflux, cooling, and acidifying with HCl. The precipitated pyrogallolcarbonic acid is filtered and recrystallized from hot water. The Ca contents of calf, goat, and steer hide, at the stages indicated, were found to be: untreated, 0.3, 0.5, 0.35%; after deliming, 0.22, 0.3, 0.15%; after bating, 0.15, 0.2, 0.15%. L.M.

Action of Perspiration on Vegetable-tanned Leathers. R. Ferebauer. *Kozarstvi*, **6**, 34–36, 54–55 (1956).—Action of perspiration on vegetable-tanned insoles was studied. The pH value of fresh human perspiration is 5.2–6.0, but that of perspiration extracted from socks worn 5 days is 6.6–8.7. The most effective artificial perspiration contained 0.05 *N* NH_4OH, 0.4% NaCl, and 0.05% α - amino - caproic acid. Chemical analyses of insoles worn for 4, 8, and 10 months are given. Ash content increased from 1.5 to 3.6% and pH value from 4.86 to 5.80, and tear strength decreased from 2.6 to 1.4 kg. per sq. mm. Surface shrinkage occurs as a result of repeated wetting by perspiration or by water at 37°C. and drying. Maximum longitudinal shrinkage after treatment with artificial perspiration for 35 days is 12.4 mm. Prechroming of vegetable-tanned insoles does not influence the deterioration. L.M.

Hydrolysis of Sole-Clipping Refuse. A. Zelinka. *Kozarstvi*, **6**, 85–87 (1956).—Sole clippings can be utilized as a low-density filler for rubber soles or rubber flooring after hydrolysis with live steam at 120°C. The product, a pale brown, resinous substance, is thermoplastic and is suitable as a filler without calendering. L.M.

Studies on Vegetable Tanning. I. Ceric Sulfate Oxidation Method for the Estimation of Vegetable Tannins. Y. Inouye and H. Okamura. *Bull. Japanese Assoc. Leather Technologists*, **3**, 12–14 (1957) (English summary).—Current methods for volumetric determination of tannin are erratic because the end point is not sharp. A new method, employing 0.1 *N* $Ce(SO_4)_2$ and *N* H_2SO_4 gives more accurate results. The accuracy is said to be nearly the same as that of the hide powder method. H.B.M.

Studies on the Selective Absorption of Chromium Complex by Hide. A. Kawamura and K. Wada. *Bull. Japanese Assoc. Leather Technologists*, **3**, 15–20 (1957) (English summary).—Cr tanning is performed by the joint action of Cr complexes of different charges. Selective absorption of Cr was studied with hide powder pretreated with $HClO_4$. The sign of the charge of the Cr complex absorbed varied with the pH value. The nature of Cr leather varies not only with the quantity but also with the kind of combined Cr in accordance with pH of the liquor. H.B.M.

Eggs for Greasing Leather. V. Kubelka and A. Blazek. *Kozarstvi*, **6**, 179–80 (1956).—Use of whole eggs, made necessary because separation of yolk and white in old eggs is difficult, must take into account the properties of both white and yolk. Hen eggs weigh 40–80 g., composed of yolk 32 (less in heavier eggs), white 57, and shell 11%. The composition of whole hen and duck eggs is: fat 12, 15; protein 12.6, 12.2; water 73, 71; and ash 1.1, 1.2%. Yolks contain water, 47–50, egg oil 20–22, protein (vitellin, livetin) 15.4–15.9, lecithin 8–10.5, cholesterol 0.5–1.6, cerebrin 0.2–0.3, ash 1.0–1.5, P 0.6, S 0.2, Cl 0.17, K 0.11, Ca 0.15, coloring matter 0.5–0.6, and dextrose 0.2%. The white contains water 86.0–86.6, protein 11.6, dextrose 0.6, ash 0.8, S 0.2, P 0.59, K 0.15, and Na 0.16%. L.M.

Suspending Hides in Deliming and Tanning Pits. B. Plechac. *Kozarstvi*, **6**, 166–70 (1956).—Methods of suspending hides or skins in connection with mechanization of tanneries are described. L.M.

Sodium Fluosilicate in the Salting of Calfskins. V. Pektor and V. Navratil. *Kozarstvi*, **6**, 149–51 (1956).—Calfskins were salted with 25, 50, and 75% salt containing 2% Na_2SiF_6. The amount of salt required proved to be more than 25 but less than 50%. Formation of red, violet, and normal salt stains was inhibited by Na_2SiF_6. The skins were evaluated after curing for 30, 90, and 180 days. Yield and quality were not impaired. The toxicity of Na_2SiO_6 was studied. Gelatin made from skins treated with 1% Na_2SiF_6 contained 130–160 p.p.m. of F, but gelatins made from normal skins contained 20–200 p.p.m., derived from lime which may contain up to 800 p.p.m. L.M.

Chlorinated Naphthalenes as Substitutes for Fats in Fatliquoring. K. Tuma. *Kozarstvi*, **6**, 134–36 (1956).—Use of a eutectic mixture of mono- and dichloronaphthalenes is proposed. This was prepared by chlorinating 100 g. napthalene with 33 g. Cl_2 at 120°–140°C. for 5–6 hr. with 0.1% powdered Fe_2O_3 as catalyst. The distillation of the product yielded 1–1.5% below 220°, 70–76% from 220° to 260°, 8–12% above 260°C., residue 7–9%. The main fraction melts at –21°C. and contains C 71.5, H 4.12, Cl 24.2, and HCl 0.0013%. The fractions distilling below 220° and above 260°C. may be further chlorinated to form an insulating material. Side upper leather was fatliquored with a mixture of the 220°–260° fraction 55, sulfated fish oil 25, mineral oil 20, soap 0.225, and sulfated lauryl alcohol 0.5%, using 5.5% of the mixture based on the shaved weight. The quality of fatliquoring is good, but the odor of naphthalene requires good ventilation of the working and drying rooms. The odor disappears permanently from the leather after several weeks' storage. The mono - dichloronaphthalene is hygienically unobjectionable, but higher chlorinated naphthalenes are poisonous. The chlorinated naphthalene has good affinity for leather, does not hydrolyze, gives a good tear resistance, and is claimed to be cheaper (in Czechoslovakia) than sulfated fish oils. A review of fat substitutes is given, stressing the importance of polar groups. L.M.

Patent Leathers on Basis of PVC. J. Drexler. *Kozarstvi*, **6**, 143–45 (1956).—Leather splits are lacquered with a film of polyvinyl chloride (PVC) applied at 160°C. The leather is cooled on the flesh side to prevent damage. Use of a highly polished ironing plate produces a high gloss. The film is composed of PVC-S 50, and plasticizer (dibutyl phthalate, ED 242, Mesamoll) 50%. The best cement for gluing the film to the surface is a combination of equal parts of Vinol H and Polysar N 60. The adhesion of the film is 7.54 kg. for a strip 14.5 x 3 cm. With pigskins the follicles show through a single coat, necessitating 2 coats. The base film, 0.3 mm. thick, is composed of butadiene - acrylonitrile copolymer 50, PVC-G 100, dioctyl phthalate 22.5, and dibutyl phthalate 22.5 parts. The second coat, 0.1 mm. thick, contains PVC-S 50, dioctyl phthalate 25, and dibutyl phthalate 25 parts. L.M.

The Evaluation of PVC Products by Measuring the Growth of Cracks. Z. Hrabel and K. Kotik. *Kozarstvi*, **6**, 163–66 (1956); see preceding abstract.—Artificial leathers based on PVC are of growing importance. They can be evaluated by studying the rate of growth of cracks at —15°C. The surface is first damaged by a needle puncture, and the number of flexes required to produce a crack 4 mm. long is determined. The samples are conditioned for 10 min. at the low temperature, then flexed and examined every 10 to 20 minutes. Pictures of the apparatus are given. The best plasticizer for PVC at low temperature is dioctyl phthalate, followed by dioctyl sebacate, butylacetyl ricinoleate, dibutyl phthalate, Palatinol AH, and Palatinol F. Tricresyl phosphate is unsuitable. This method can also be used to follow and control the degree of polymerization of a PVC batch. L.M.

Complex Compound of Chromium with Aspartic Acid. L. M. Volshtein, G. G. Motyagina, and L. S. Anakhova. *Zhur. Neorg. Khim.*, **1**, 2378–84 (1956); *Chem. Abstr.*, **51**, 5618*e*.

Determination of the Composition of the Green Chromium Bromide by the Argentometric Method. Y. P. Nazarenko and R. S. Khaimovich. *Zhur. Neorg. Khim.*, **1**, 1758–65 (1956); *Chem. Abstr.*, **51**, 5634*f*.

Direct Titration of Sulfate. M. Q. Freeland and J. S. Fritz. *U. S. Atomic Energy Comm. ISC-667*, 1–32 (1956); *Chem. Abstr.*, **51**, 5637*f*.

Formaldehyde Condensations with Phenol and Its Homologs. XVIII. Chromatographic Analysis. S. R. Finn and J. W. James. *J. Appl. Chem.* (London), **6**, 466–76 (1956); *Chem. Abstr.*, **51**, 5637*i*.

Determination of Amino Acids by Paper Chromatography. A Solvent to Replace Phenol. M. Wolf. *Biochim. et Biophys. Acta*, **23**, 186–91 (1957) (in English); *Chem. Abstr.*, **51**, 5639*i*.

Modifications in Collagen - Mucopolysaccharide Combinations Brought about in *Vitro* by Various Salts. S. Bazin and A. Delaunay. *Compt. Rend.*, **243**, 1942–44 (1956); *Chem. Abstr.*, **51**, 5860*i*.

Colorimetric Method for Determining Aliphatic Amines in the Presence of Ammonia. L. Ekladious and H. K. King. *Biochem. J.*, **65**, 128–31 (1957); *Chem. Abstr.*, **51**, 5880*g*.

Swelling of Gelatin Films. Effects of Drying Temperature and of Conditioning the Layers in Atmospheres of High Relative Humidity. D. W. Jopling. *J. Appl. Chem.* (London), **6**, 79–84 (1956); *Chem. Abstr.*, **51**, 6196*b*.

A Method of Isolation of a Cuticle Sheath from Wool Fibers. R. E. Elliott and J. B. Roberts. *J. Soc. Dyers and Colourists*, **73,** 95–97 (1957).—Oxidation of wool with acid $K_2Cr_2O_7$ solution, followed by extraction with dilute NH_4OH, leaves a residue of high sulfur content. This residue comprises at most 2% of the weight of the original wool, and microscopic investigations have revealed that it is a cuticle sheath consisting of epicuticle and endocuticle. Electron-microscopic examination of the endocuticle has shown that it is composed of fibrils 0.15 microns in diameter, each fibril being built up of microfibrils 0.05 microns in diameter. The sulfur content of the dichromate ammonia resistant cuticle sheath is appreciably higher than that of the complete wool fiber. The sulfur is present as cystine, but the resistance of the cystine in the cuticular layer to dichromate oxidation is unexplained. R.M.L.

Resin Finishes for Upper Leather. V. Pektor and L. Dvoranek. *Kozarstvi*, **6,** 87–89 (1956).—The elongation at break was measured for 0.1 mm. films of resins, formed by spraying on glass, and the effect of adding other finishing materials was studied. The elongation of a mixture of butyl methacrylate and butyl acrylate (4 : 1) was lowered by adding more than 15% of a casein finish, and with 30% added the film was brittle. Addition of a casein-wax mixture had less effect. The elongation of this resin increased with temperature. The resin is stable to ultraviolet light. A pure polyethacrylate film elongated by 1000%, compared to 600% for the butyl acrylate - methyacrylate mixture, but the elongation dropped to 448 and 178% respectively when 10 and 20% casein was added. The polyethacrylate elongation was less affected by temperature than that of the butyl polymer. A mixture of polymethacrylate and dibutyl phthalate (9 : 1) showed elongation exceeding 1000%, and elongation was less affected by adding casein or wax-casein than those of the resins previously discussed. In contrast with the previous resins the elongation increased at lower temperatures. Effects of adding white pigments (TiO_2 dispersed with casein) are discussed. Formulas are given for finishing various kinds of leathers.
L.M.

Final Purification of Tannery Effluents. V. Kubelka and C. Halamek. *Kozarstvi*, **6,** 93–96 (1956).—Simple sedimentation is not enough because dilution in the receiving streams is inadequate. Proper sedimentation removes 26% of the total solids, 24% organic solids, 16% oxidizable matter, 33% of total N, and lowers the BOD by 33.5%. Treatment before sedimentation with 0.1 g. per l. of $Al_2(SO_4)_3 \cdot 12H_2O$ plus H_2SO_4 to give pH 7 increases the above figures to 41, 63, 67, and 66% (no figure given for BOD). Purification by $FeSO_4$ is possible without neutralization if the sewage is first oxidized with Cl_2, which is expensive. Electrocoagulation was studied and found to be less effective. The sludge can be dried, in beds not over 1 foot deep, to 70–80% water. The sludge amounts to about 10% by volume of the effluent and to about 130 g. per kg. of salted hide weight. Its pH falls from 11 to about 7 on drying. It contains about 10% CaO and 2–3% N. When transportation costs are not prohibitive, it can be used on farms by first mixing it with manure and storing for several months to decompose tannins. Anthrax spores are entrapped by the sludge and not found in the effluent. The purification apparently destroys or inactivates the spores, as tests for anthrax pores on 100 sludge samples, some

of them from tanneries using suspected anthrax hides, all were negative. The sewage contains 30–40% of the nitrogenous matter of the oroginal hides, 30% of the tannin, and 50–60% of the Cr used. Hair should be removed from the sewage, and spent Cr liquors should be regenerated, but recovery of other by-products is not economically practicable. L.M.

The Amino Acid Composition of Fish Collagen and Gelatin. J. E. Eastoe. *Biochem. J.*, **65.** 363–68 (1957).—The amino acid composition of collagen from a few species representing a zoologically wide range of fish types was determined by column chromatography. Sturgeon swim-bladder collagen, cod bone gelatin, sharkskin gelatin, and lungfish collagen and gelatin showed a similar amino acid distribution to mammalian collagen, with decreased amounts of proline and hydroxyproline and increased serine, threonine, and in some cases methionine and hydroxylysine. Gelatin prepared from cod bone had a very low rigidity at 10°C., whereas sturgeon, shark, and lungfish collagens gave gelatins having rigidities of the same order as, but probably somewhat below, those of mammalian gelatins. In general, the shrink temperature of the collagen and gel properties of extracted gelatin decrease with decreasing hydroxyproline content. Certain departures in detail from this behavior indicate that other unknown features of composition may influence the stability of linkages between polypeptide chains. Variations in properties and composition of fish collagens seem related to water temperature of normal habitat rather than to considerations of broad zoological classification. J.M.C.

Connective Tissue Growth Stimulated by Carrageenin. I. The Formation and Removal of Collagen. D. S. Jackson. *Biochem. J.*, **65,** 277–84 (1957.—Large amounts of easily separated connective tissue are produced upon injection of carrageenin subcutaneously into the lower abdominal regions of guinea pigs. The occurrence in this tissue of acid-soluble collagen, neutral salt solution–soluble collagen, and insoluble collagen was determined. The incorporation of labeled glycine into these fractions was also studied. Maximum wet weight of new tissue was produced after 7–9 days. Most of the insoluble collagen was formed between 5 and 9 days. The neutral salt solution–soluble collagen appeared before acid-soluble collagen and increased in concentration up to the fifth day, remaining constant and then increasing rapidly as the tissue was resorbed. The concentration of acid-soluble collagen increased throughout the experimental period. Maximum activity of labeled glycine was found in neutral salt solution–soluble collagen after 10 hours. Neutral salt solution–soluble collagen is a precursor of collagen fibers and can be transformed into acid-soluble collagen or add on to pre-existing acid-soluble collagen and insoluble collagen. A water-soluble protein containing hydroxyproline was also found. J.M.C.

The Influence of the Duration of Pickling and Methods of Chrome Tanning on the Properties of Chrome Side Leather. M. F. Chambers, R. G. Mitton, and E. F. Nattrass. *J. Soc. Leather Trades' Chemists*, **41,** 60–69 (1957).—The effects of time (5 min. or 3 days) in pickle solution, of basicity (33, 42, and 50%), and of procedure by which chrome is added (all at once

or in two stages) were studied in preparation of chrome side leather. Grease and chrome contents were determined and measurements made of area, thickness, density, resistance to compression, buckle-tear strength, dye penetration, and colorfastness to rubbing. Chrome fixation was increased when tannage was begun in liquor of higher basicity, and this increase was greatest if a short pickling period was employed. Regardless of basicity, the short pickling period resulted in thinner leather. This result was partly compensated for by a greater area yield. Density, buckle-tear strength, and resistance to compression were not greatly influenced by any of the factors which were varied. J.M.C.

The Vegetable Tannage of Sheepskins: A Systematic Study of Various Factors in the Tanning Process. II. Chemical Analysis, Manual Assessments, and Darkening of the Leathers on Exposure to Light. M. F. Chambers, R. G. Mitton, and E. F. Nattrass. *J. Soc. Leather Trades' Chemists*, **41**, 48–59 (1957).—Vegetable-tanned sheepskins which were brought to the tan liquors by a series of varied pretreatments (see *JALCA*, **52**, 295) were chemically analyzed and assessed manually by experts. Higher degrees of tannage were obtained with wattle than with chestnut, and with the more concentrated tannin solutions. Degree of tannage varied in a complex manner with acid and salt content of the tan liquor. The greatest fullness and firmness were otained with liquors of low pH and low salt content but at the expense of a greater tendency to drawn grain, particularly when the tan liquors were concentrated. The depth of color was determined of leathers tanned at various pH values with varying salt contents and subsequently exposed to ultraviolet radiation for periods up to 18 hr. Chestnut tannage with low pH and salt content gives a leather the shade of which is not altered by exposure to light. **III. The Physical Properties of Leathers.** M. F. Chambers, R. G. Mitton, and E. F. Nattrass. *J. Soc. Leather Trades' Chemists*, **41**, 94–105 (1957).—An account is given of the results of physical and mechanical tests made on the sheepskin leathers whose tannages and chemical analyses were described in earlier papers. Even though the acid and salt contents of the wattle and chestnut tan liquors were adjusted to equality and both were used at similar concentrations, the resulting chestnut leather was much firmer and stiffer, although thinner and of smaller area. Application of a soft or firm dressing in finishing affected the properties materially. Only slight differences were noted between the pickled and nonpickled skins. Major changes in properties resulted from variation of both salt content and pH during tannage, particularly if both were low. Contour diagrams are presented to relate relative areas, weight yields, thickness, resistance to compression, tensile strength, and buckle tear strength with pH and salt content of tannage. J.M.C.

The Tanning Characteristics of Aliphatic Aldehyde-Ketone Resins. J. R. B. Hastings and T. White. *J. Soc. Leather Trades' Chemists*, **41**, 37–48 (1957).—The alkali-catalyzed reaction between aliphatic aldehydes and ketones produces condensates which can be resinified by further treatment with alkali. The tanning characteristics of these aldehyde-ketone materials were studied (1) by impregnation of hide with a primary condensation product which was then resinified *in situ* and (2) by a conventional tanning technique. Water-soluble condensates were prepared from acetone–HCHO, methyl ethyl ketone–HCHO,

methyl propyl ketone–HCHO, acetone–CH_3CHO, methyl ethyl ketone–CH_3CHO, and acetone-crotonaldehyde. Resinification of initial condensate *in situ* in oxhide (butt portion) required one day in 10% w/v Na_2CO_3 solution. After resinification excess alkali was removed by washing. Resin contents as high as 20% were obtained by this procedure, and shrink temperature was raised a maximum of 14°C. Conventional methods of tanning were applied by converting the condensates to water-soluble resins by treatment with alkali sulfite or bisulfite. Tanning was initiated at pH 4–5 with a gradual drop in pH toward pH 3 occurring with increased concentration. Tanning with these products gave a range of leathers cream to orange in color, with shrink temperature raised as much as 50°C. and with degree of tannage as high as 60. In general, the lower the degree of sulfiting or bisulfiting, the fuller was the resulting leather. While sulfited and bisulfited resins are indicated to have very limited potentialities as tanning agents if used alone, they should have considerable use as filling or dispersing agents when used in conjunction with other tanning materials. Difficulties encountered in the analysis of solubilized resin content by official S. L. T. C. methods are discussed. J.M.C.

Warble Fly Eradication Experiments. V. Kubelka, J. Tamchyna, and E. Markusovka. *Kozarstvi*, **6**, 73–76 (1956).—Results of application of a 1–2% solution of "Bovinol"—a mixture of hexachlorocyclohexane, DDT, and an emulsifier—are reported. The index of warble infestation (1–10 maggots = 5, 11–20 = 15, 20–100 = 60, over 100 = 100) was lowered from 8 to 3.6 for all cattle, about half of whom were infected. L.M.

Staining of Insoles in Contact with Polyvinyl Chloride Artificial Leather. Z. Hrabal and K. Kotik. *Kozarstvi*, **6**, 85–86 (1956).—Staining was traced to solution of syntans in softeners in the PVC artificial leather, especially dibutyl phthalate, producing a dirty brown stain. Natural tannins do not produce such stains. Latex cements do not prevent the staining. L.M.

Evaluation of Raw Oils for the Manufacture of Fat Liquors. V. Pilc. *Kozarstvi*, **6**, 68–70 (1956).—Animal or vegetable oils to be sulfonated should have I_2 value from 90 to 120, except sperm oil which has I_2 value 70 because it contains fatty alcohols. Mixtures of oils having I_2 value in this range are less suitable than single oils. Solid fat value should not exceed 18, preferably 8–12. Other recommended standards include acid no., max. 30; fat acids + unsaponifiables, 92%; unsaponifiables, max. 7%; ash, max. 1%; water, max. 0.5%. A standard laboratory sulfonation test, for which details are given, is essential. L.M.

The Present and Future Scope of Peptide Synthesis. G. W. Kenner. *J. Soc. Leather Trades' Chemists*, **41**, 75–86 (1957.—This is the Seventh Proctor Memorial Lecture. Synthetic organic chemistry can provide large polypeptides of definite structure for use as models of proteins and can make available small peptides which may be used in studying protein reactions. A review of reactions involved in peptide synthesis is presented. J.M.C.

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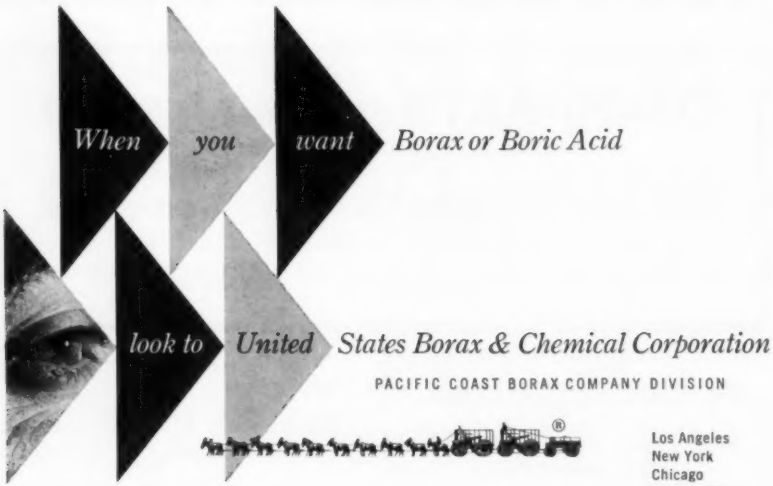

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INDEX TO ADVERTISERS

ADOLF SCHUBERT XXXIII
AMERICAN EXTRACT CO. XXXIV
APEX CHEMICAL CO., INC. XXXIV
ARKANSAS COMPANY, INC. VI
ARMOUR LEATHER CO. XXXIII
ARTHUR C. TRASK CO. XXXI
ARTHUR THOMAS CO. XX
ATLAS REFINERY XVI
AULSON TANNING MACHINERY CO., THE XXXIII
BARKEY IMPORTING CO., INC. ..... X — XIV
BARRENTAN CORPORATION XXXIV
BONA ALLEN, INC. XXXVI
BORNE CHEMICAL COMPANY, INC. XXIII
BUCKMAN LABORATORIES, INC. IV
DIAMOND ALKALI CO. IX
CHEMTAN COMPANY XIX
EISENDRATH TANNING CO. XXV
E. F. DREW & CO., INC. XXXVI
EUROPEAN MANUFACTURERS OF CHESTNUT EXTRACTS XXVIII
FRANK CRYSTAL ..... Outside Back Cover
FRANK F. MARSHALL XXXI
GARDEN STATE TANNING INC. XXXI
HOOKER ELECTROCHEMICAL CO. XI
HOWES LEATHER CO., INC. XXXVI
INTERNATIONAL PRODUCTS CORP. XII
KEPEC CHEMICAL CORPORATION XXXI
LEATHER AND SHOES V
LEATHER MANUFACTURER, THE XXIX
L. H. LINCOLN & SON, INC. XVII
MARDEN WILD CORPORATION XXIV
MUTUAL CHROMIUM CHEMICALS, ALLIED CHEMICAL & DYE CORP. ..... Inside Back Cover
NEWARK LEATHER FINISH CO. XXXII
NOPCO CHEMICAL CO. XXI
OHIO LEATHER CO., THE XXV
OLSON IMPORTING COMPANY, INC., THE ..... Inside Front Cover
ORTHMANN LABORATORIES, INC., THE XXV
PRESTO COLOR CO. XXVI
PROCTOR AND SCHWARTZ, INC. XXXV
REILLY-WHITEMAN-WALTON CO. XXIX
ROBESON PROCESS CO. II
ROHM & HAAS VIII
SALEM OIL & GREASE CO. XXX
SAXE CUTCH CORPORATION XXIV
SHOE & LEATHER REPORTER XXX
SOLVAY PROCESS DIVISION, ALLIED CHEMICAL & DYE CORP. XXVII
SOUTH AFRICAN WATTLE EXTRACT MFRS. ASSO. XV
SUN OIL COMPANY XXV
TANEXCO, INC. XXXV
TANIMEX CORPORATION III
TANNER'S COUNCIL RESEARCH LABORATORY ..... XXXI—XXXVI—XXXVII
UNITED STATES BORAX & CHEMICAL CORP. XXVI
UNITED STATES RUBBER COMPANY XIII
UNITED STATES TESTING COMPANY XXXII
WALLERSTEIN COMPANY, INC. XXII
WARNER CO. XXIV
WHITTEMORE-WRIGHT CO. XXVI
WOLF, JACQUES & CO. VII
YOUNG CO., J. S. XVIII

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